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United States
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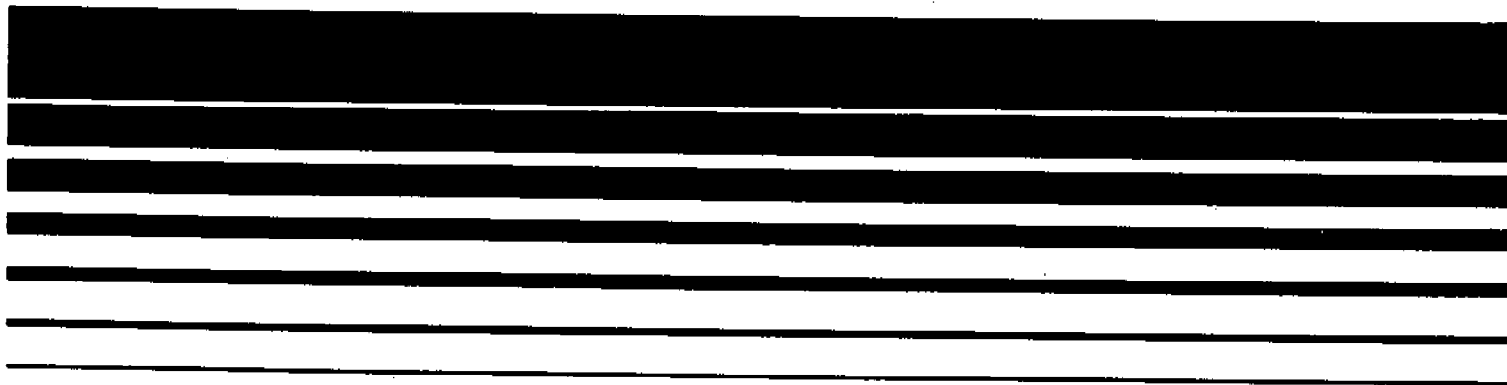
Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/4-91-008
January 1991

Air



**1990 NONMETHANE
ORGANIC COMPOUND
AND
THREE-HOUR
AIR TOXICS MONITORING
PROGRAM**





1990 NONMETHANE ORGANIC COMPOUND AND THREE-HOUR AIR TOXICS MONITORING PROGRAM

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Office Of Air And Radiation
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

January 1991



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EPA-450/4-91-008



TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
LIST OF FIGURES.	vii
LIST OF TABLES.	x
SYMBOLS AND ABBREVIATIONS	xiii
1.0 SUMMARY AND CONCLUSIONS	1-1
1.1 NMOC MONITORING PROGRAM	1-2
1.1.1 Introduction and Data Summary	1-2
1.1.2 Calibration and Drift	1-5
1.1.3 Precision	1-5
1.1.4 Accuracy.	1-5
1.1.5 Other Quality Assurance Measurements	1-6
1.2 THREE-HOUR AIR TOXICS MONITORING PROGRAM	1-16
1.2.1 Overall Data Summary	1-16
1.2.2 Site Results	1-16
1.2.3 Gas Chromatography/Mass Spectrometry Confirmation Results	1-17
1.2.4 Precision	1-17
1.2.5 External Audit	1-17
2.0 NMOC DATA SUMMARY.	2-1
3.0 NMOC TECHNICAL NOTES	3-1
3.1 NMOC FIELD SAMPLING EQUIPMENT	3-1
3.1.1 Installation	3-1
3.1.2 Operation	3-3
3.1.3 Troubleshooting Instructions	3-4
3.1.4 Sampler Performance for 1990	3-6
3.1.5 Field Documentation	3-7
3.2 NMOC ANALYSIS.	3-7
3.2.1 Instrumentation	3-7
3.2.2 Hewlett-Packard Model 5880 Gas Chromatograph Operating Conditions	3-7
3.2.3 NMOC Analytical Technique	3-10
3.3 CANISTER CLEANUP SYSTEM	3-10
3.3.1 Canister Cleanup Equipment	3-12
3.3.2 Canister Cleanup Procedures	3-14

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
4.0 NMOC QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES	4-1
4.1 INTRODUCTION AND CONCLUSIONS	4-1
4.2 CALIBRATION AND INSTRUMENT PERFORMANCE	4-2
4.2.1 Performance Assessment	4-2
4.2.2 Calibration Zero, Span, and Drift	4-2
4.2.3 Calibration Drift	4-8
4.3 IN-HOUSE QC SAMPLES	4-18
4.4 REPEATED ANALYSES	4-24
4.4.1 Site Sample Results	4-27
4.4.2 Local Ambient Samples	4-31
4.5 DUPLICATE SAMPLE RESULTS	4-37
4.5.1 Analytical Precision	4-44
4.5.2 Components of Variance	4-44
4.6 CANISTER PRESSURE RESULTS	4-52
4.7 CANISTER CLEANUP RESULTS	4-52
4.8 EXTERNAL AUDIT RESULTS	4-55
4.9 DATA VALIDATION.	4-55
4.10 NMOC MONITORING PROGRAM RECORDS	4-62
4.10.1 Archives.	4-63
4.10.2 Magnetic Disks	4-63
5.0 NMOC DATA ANALYSIS AND CHARACTERIZATION	5-1
5.1 OVERALL CHARACTERIZATION	5-1
5.2 MONTHLY VARIATIONS, 1984 - 1990	5-3

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
6.0 RECOMMENDATIONS, NMOC MONITORING PROGRAM	6-1
6.1 SITING CRITERIA	6-1
6.2 OPERATING PROCEDURE CHANGES	6-1
6.3 VERTICAL STRATIFICATION STUDY	6-1
6.4 SEASONAL NMOC STUDIES	6-2
6.5 DIURNAL STUDIES.	6-2
6.6 CANISTER CLEANUP STUDIES	6-2
6.7 COORDINATED SAMPLING AT NMOC SITES	6-3
6.8 FIELD AUDIT.	6-3
6.9 DUPLICATE SAMPLE AND REPLICATE ANALYSIS	6-4
7.0 THREE-HOUR AIR TOXICS DATA SUMMARY	7-1
7.1 OVERALL RESULTS.	7-1
7.2 SITE RESULTS	7-4
8.0 THREE-HOUR AIR TOXICS TECHNICAL NOTES	8-1
8.1 SAMPLING EQUIPMENT AND INTERFACE	8-1
8.2 THREE-HOUR AIR TOXICS SAMPLING CERTIFICATION	8-1
8.2.1 Sampler Certification Blanks - Humidified Zero Air	8-3
8.2.2 Sampler Certification Challenge - Selected Target Compound	8-3

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
8.3 STANDARDS GENERATION	8-3
8.4 CALIBRATION ZERO AND SPAN	8-8
8.5 GAS CHROMATOGRAPH/MULTIDETECTOR ANALYSIS AND COMPOUND IDENTIFICATION	8-8
8.6 GAS CHROMATOGRAPH/MASS SPECTROMETER ANALYSIS AND COMPOUND IDENTIFICATION CONFIRMATION	8-8
8.7 QA/QC DATA	8-10
8.7.1 GC/MD and GC/MS Method Detection Limits	8-10
8.7.2 Repeated Analyses	8-10
8.7.3 Duplicate Sample Results	8-13
8.7.4 GC/MS Confirmation Results	8-13
8.7.5 External Audits	8-13
8.8 DATA RECORDS	8-19
9.0 RECOMMENDATIONS, THREE-HOUR AIR TOXICS PROGRAM	9-1
9.1 COMPOUND STABILITY STUDIES	9-1
9.2 CANISTER CLEANUP STUDIES	9-1
9.3 CARBONYL STUDIES	9-2
10.0 CARBONYL SAMPLING, ANALYSIS, AND QUALITY ASSURANCE PROCEDURES	10-1
10.1 SAMPLING EQUIPMENT AND PROCEDURES	10-1
10.2 ANALYTICAL PROCEDURES	10-3
10.3 QUALITY ASSURANCE PROCEDURES	10-4
10.4 CALIBRATION PROCEDURES	10-4
10.4.1 Daily Quality Control Procedures	10-4
10.4.2 Duplicate Samples	10-4
10.4.3 Trip Blanks	10-6
10.4.4 Precision	10-6
10.4.5 Practical Quantitation Limit	10-6

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
10.5 RESULTS.	10-6
10.5.1 Formaldehyde Control Standards	10-11
10.5.2 Recoveries of Spikes	10-11
10.5.3 Blanks.	10-15
11.0 REFERENCES	11-1

APPENDICES

APPENDIX A: SAMPLING SITES FOR 1990 NMOC MONITORING PROGRAM

APPENDIX B: CRYOGENIC PRECONCENTRATION AND DIRECT FLAME
IONIZATION DETECTION (PDFID) METHOD

APPENDIX C: 1990 NMOC MONITORING PROGRAM SITE DATA

APPENDIX D: 1990 NMOC MONITORING PROGRAM INVALIDATED AND MISSING
SAMPLES

APPENDIX E: PDFID INTEGRATOR PROGRAMMING INSTRUCTIONS

APPENDIX F: 1990 NMOC DAILY CALIBRATION DATA

APPENDIX G: 1990 NMOC IN-HOUSE QUALITY CONTROL SAMPLES

APPENDIX H: MULTIPLE DETECTOR SPECIATED THREE-HOUR SITE DATA SUMMARIES

LIST OF FIGURES

<u>Number</u>		<u>Page</u>
1-1	In-house propane QC results Channel A	1-7
1-2	In-House propane QC results Channel B	1-8
1-3	In-house propane QC results Channel C	1-9
1-4	In-House propane QC results Channel D	1-10
1-5	Orthogonal regression comparing QAD with Radian NMOC analyses	1-14
3-1	Sampling system for collecting 3-hour integrated ambient air samples	3-2
3-2	NMOC sampling field data form	3-5
3-3	NMOC invalid sample form	3-8
3-4	NMOC analytical equipment	3-11
3-5	Canister cleanup apparatus	3-13
4-1	NMOC performance results, Channel A	4-4
4-2	NMOC performance results, Channel B	4-5
4-3	NMOC performance results, Channel C	4-6
4-4	NMOC performance results, Channel D	4-7
4-5	Daily calibration zero, Channel A	4-9
4-6	Daily calibration zero, Channel B	4-10
4-7	Daily calibration zero, Channel C	4-11
4-8	Daily calibration zero, Channel D	4-12
4-9	Daily calibration span, Channel A	4-13

LIST OF FIGURES (Continued)

<u>Number</u>		<u>Page</u>
4-10	Daily calibration span, Channel B	4-14
4-11	Daily calibration span, Channel C	4-15
4-12	Daily calibration span, Channel D	4-16
4-13	In-house quality control results, Channel A	4-19
4-14	In-house quality control results, Channel B	4-20
4-15	In-house quality control results, Channel C	4-21
4-16	In-house quality control results, Channel D	4-22
4-17	Orthogonal regression comparing QAD with Radian NMOC analyses	4-28
4-18	95% Confidence intervals for mean NMOC difference	4-39
4-19	Audit bias, Radian Channel A vs. EPA-QAD	4-57
4-20	Audit bias, Radian Channel B vs. EPA-QAD	4-58
4-21	Audit bias, Radian Channel C vs. EPA-QAD	4-59
4-22	Audit bias, Radian Channel D vs. EPA-QAD	4-60
5-1	Stem-and-leaf plot of the 1990 NMOC data	5-2
5-2	Stem-and-leaf plot for the ln(NMOC) data	5-4
5-3	Cumulative frequency distribution for 1990 NMOC data	5-5
5-4	Cumulative frequency distribution for 1990 ln(NMOC) data	5-6
5-5	Stem-and-leaf plot of the NMOC data for June, 1990	5-9
5-6	Stem-and-leaf plot of the NMOC data for July, 1990	5-10

LIST OF FIGURES (Continued)

<u>Number</u>		<u>Page</u>
5-7	Stem-and-leaf plot of the NMOC data for August, 1990	5-11
5-8	Stem-and-leaf plot of the NMOC data for September, 1990	5-12
5-9	Monthly mean NMOC emissions for 1985 through 1990	5-13
8-1	Gas chromatographic multidetector system	8-2
8-2	Dynamic flow dilution apparatus	8-7
8-3	Air toxics multiple detector system	8-9
10-1	3-Hour carbonyl sampling subsystem	10-2
10-2	Field data and custody form	10-5

LIST OF TABLES

<u>Number</u>		<u>Page</u>
1-1	1990 NMOC COMPLETENESS RESULTS	1-3
1-2	1990 NMOC SITE STATISTICS	1-4
1-3	LINEAR REGRESSION PARAMETERS FOR IN-HOUSE QUALITY CONTROL DATA	1-11
1-4	AUDIT SAMPLE RESULTS, PERCENT BIAS	1-12
1-5	AUDIT SAMPLE RESULTS, ABSOLUTE PERCENT BIAS	1-13
1-6	ORTHOGONAL REGRESSION PARAMETERS FOR COMPARATIVE ANALYSES OF SITE SAMPLES	1-15
2-1	1990 NMOC COMPLETENESS RESULTS	2-2
2-2	1990 NMOC SITE STATISTICS	2-4
2-3	1990 NMOC LOGNORMAL STATISTICS	2-5
3-1	SUPPORT GAS OPERATING CONDITIONS	3-9
4-1	1990 PERFORMANCE ASSESSMENT SUMMARY, RADIAN CHANNELS . .	4-3
4-2	SUMMARY NMOC CALIBRATION FACTOR DRIFT RESULTS	4-17
4-3	LINEAR REGRESSION PARAMETERS FOR IN-HOUSE QUALITY CONTROL DATA	4-23
4-4	IN-HOUSE QUALITY CONTROL STATISTICS, BY RADIAN CHANNEL	4-25
4-5	OVERALL IN-HOUSE QUALITY CONTROL STATISTICS	4-26
4-6	ORTHOGONAL REGRESSION PARAMETERS FOR REPEATED ANALYSES OF SITE SAMPLES	4-29
4-7	SUMMARY STATISTICS OF COMPARATIVE ANALYSES FOR RADIAN VS. QAD CHANNELS	4-30
4-8	SUMMARY STATISTICS OF COMPARATIVE ANALYSES FOR RADIAN VS. QAD CHANNELS, BY RADIAN CHANNELS	4-32

LIST OF TABLES (Continued)

<u>Number</u>		<u>Page</u>
4-9	OVERALL STATISTICS FOR LOCAL AMBIENT SAMPLES	4-33
4-10	SUMMARY STATISTICS LOCAL AMBIENT SAMPLES, BY CHANNEL PAIR	4-34
4-11	LOCAL AMBIENT SAMPLES CONFIDENCE INTERVALS	4-38
4-12	DUPLICATE SAMPLES FOR 1990	4-40
4-13	REPLICATE ANALYSES FOR THE 1990 NMOC MONITORING PROGRAM . .	4-45
4-14	ANOVA FOR DUPLICATE SAMPLES 1 THROUGH 15	4-48
4-15	ANOVA FOR DUPLICATE SAMPLES 16 THROUGH 59	4-49
4-16	COMPONENTS OF VARIANCE, NMOC SAMPLING AND ANALYSIS	4-51
4-17	NMOC PRESSURE STATISTICS	4-53
4-18	PRESSURE DISTRIBUTION OF NMOC AMBIENT AIR SAMPLES	4-54
4-19	1990 NMOC AUDIT SAMPLE RESULTS	4-56
4-20	AUDIT SAMPLES, RELATIVE TO EPA-QUALITY ASSURANCE DIVISION (QAD) RESULTS	4-61
5-1	SUMMARY STATISTICS FOR 1990 NMOC SITES, BY MONTH	5-7
7-1	THREE-HOUR AMBIENT AIR SAMPLES AND ANALYSES	7-2
7-2	COMPOUND IDENTIFICATION WITH GC/MD FOR ALL 3-HOUR SITES	7-3
7-3	FREQUENCY OF OCCURRENCE OF TARGET COMPOUNDS IN 3-HOUR AMBIENT AIR SAMPLES	7-5
7-4	COMPOUND IDENTIFICATIONS WITH GC/MD BY SITE CODE	7-6

LIST OF TABLES (Continued)

<u>Number</u>		<u>Page</u>
8-1	SAMPLER CERTIFICATION ZERO RESULTS	8-4
8-2	SAMPLER CERTIFICATION CHALLENGE RESULTS	8-5
8-3	METHOD DETECTION LIMITS FOR 3-HOUR AIR TOXICS COMPOUNDS	8-11
8-4	3-HOUR AIR TOXICS REPLICATE ANALYSES BY GC/MD	8-12
8-5	SINGLE COMPOUND IDENTIFICATIONS OF GC/MD REPLICATE SAMPLE ANALYSES	8-14
8-6	THREE-HOUR AIR TOXICS DUPLICATE SAMPLE ANALYSES BY GC/MD .	8-15
8-7	GC/MD 3-HOUR AIR TOXICS DUPLICATE PRECISION BY COMPOUND .	8-16
8-8	SINGLE COMPOUND IDENTIFICATIONS OF GC/MD DUPLICATE SAMPLE ANALYSES	8-17
8-9	COMPOUND IDENTIFICATION CONFIRMATION	8-18
10-1	PRACTICAL CARBONYL QUANTITATION LIMIT	10-7
10-2	CARBONYL RESULTS FOR BATON ROUGE, LA (BRLA)	10-8
10-3	CARBONYL RESULTS FOR NEWARK, NJ (NWNJ)	10-9
10-4	CARBONYL RESULTS FOR PLAINFIELD, NJ (PLNJ)	10-10
10-5	CARBONYL LABORATORY REPLICATES	10-12
10-6	ANALYSIS OF QUALITY CONTROL STANDARDS	10-13
10-7	FORMALDEHYDE LABORATORY SPIKES	10-14
10-8	FIELD SPIKE RECOVERIES OF FORMALDEHYDE	10-16
10-9	CARBONYL SPIKE RECOVERIES	10-17
10-10	CARBONYL LABORATORY BLANKS	10-18
10-11	CARBONYL FIELD BLANKS	10-19

SYMBOLS AND ABBREVIATIONS

AC, or A.C.	area counts, generated from a gas chromatograph
ADELTA	absolute value of DELTA
ADIF	absolute value of DIF
ADIFF	absolute value of DIFF
AIRS	Aerometric Information Retrieval System
a.m.	ante meridiem
APDIFF	absolute value of PDIFF
APDIF	absolute value of PDIF
APR	April
AREAL	Atmospheric Research and Exposure Assessment Laboratory
Aug	August
Bldg.	building
BMTX	Beaumont, TX - AIRS No. 48-245-0009
Cal., or Calib.	calibration
cm	centimeter
CRM	Certified Reference Material
DELTA	Radian NMOC concentration - QAD NMOC concentration, ppmC; Radian NMOC concentration - ASRL concentration, ppmC; or AREAL NMOC concentration - QAD NMOC concentration, ppmC
DIF	(NMOC concentration for the second channel) - (NMOC concentration for the first channel
DIFF	measured NMOC concentration - calculated NMOC concentration ppmC for in-house quality control samples
Dup.	duplicate
e	base of natural logarithm, 2.71828...
ECD	electron capture detector
EPA	United States Environmental Protection Agency
F	Friday
FID	flame ionization detector

(Continued)

SYMBOLS AND ABBREVIATIONS (continued)

GC/ECD	gas chromatography electron capture detection
GC/FID	gas chromatography flame ionization detection
GC/MD	gas chromatography multidetection
GC/MS	gas chromatography mass spectrometry
H	Thursday
Hg	mercury
HTCT	Hartford, CT - AIRS No. 09-003-1003
i.d.	inside diameter
ID	identification
INST.	instrument
Jul	July
Jun	June
L	liter
LIN	Hempstead, NY (Long Island) - AIRS No. 36-059-0005
Lpm	liters per minute
m	meter
M	Monday
MAX	maximum
μ g	microgram
MID	multiple ion detection
MIN	minimum
min.	minute
mL	milliliter
mm	millimeter
MNY	New York, NY - AIRS No. 36-061-0010
MU	mean of $\ln(\text{NMOC})$
NC	North Carolina
NIST	National Institute of Standards and Technology
NMOC	Nonmethane organic compound
NO _x	oxides of nitrogen
NWNJ	Newark, NJ - AIRS No. 34-013-0011

(Continued)

SYMBOLS AND ABBREVIATIONS (continued)

Oct	October
o.d.	outside diameter
Off.	Office
PCDIFF	percent difference = $\text{DIFF} / \text{calculated NMOC concentration} \times 100$, for in-house QC samples
PDELTA	$\frac{\text{DELTA}}{[(\text{Radian NMOC concentration} + \text{QAD NMOC concentration})/2]} \times 100;$ $\frac{\text{DELTA}}{[(\text{Radian NMOC concentration} + \text{AREAL NMOC concentration})/2]} \times 100;$ or, $\frac{\text{DELTA}}{[(\text{AREAL NMOC concentration} + \text{QAD NMOC concentration})/2]} \times 100$
PDFID	preconcentration, direct flame ionization detection
PDIF	$\text{DIF} / [(\text{NMOC concentration, 1st channel}) + (\text{NMOC concentration, 2nd channel})] / 2 \times 100$
PLNJ	Plainfield, NJ - AIRS No. 34-035-1001
p.m.	post meridiem
ppb	parts per billion
ppbv	parts per billion by volume
ppm	parts per million
ppmC	parts per million by volume as carbon
ppmv	parts per million by volume
psi	pounds (force) per square inch
psig	pounds (force) per square inch gauge
QA	quality assurance
QAD	Quality Assurance Division (EPA)
QAPP	Quality Assurance Project Plan
QC	quality control
RAO	Radian analysis order: RAO = 1 for the local ambient duplicate sample analyzed first by Radian; RAO = 2 for the local ambient duplicate sample analyzed first by EPA
RT	retention time
RTP	Research Triangle Park

(Continued)

SYMBOLS AND ABBREVIATIONS (continued)

SAROAD	Storage and Retrieval of Aerometric Data
Sep	September
SOP	standard operating procedure
SOx	oxides of sulfur
SRM	Standard Reference Material
SIGMA	standard deviation of ln(NMOC)
STD. DEV., SD	standard deviation
T	Tuesday
UATMP	Urban Air Toxics Monitoring Program
ug	microgram
U.S.	United States
UTM	Universal Transverse Mercator
W	Wednesday
°C	degrees Celsius
°F	degrees Fahrenheit
%CV	percent coefficient of variation

1.0 SUMMARY AND CONCLUSIONS

In certain areas of the country where the National Ambient Air Quality Standard (NAAQS) for ozone is being exceeded, additional measurements of ambient nonmethane organic compounds (NMOC) are needed to assist the affected states in developing revised ozone control strategies. Because of previous difficulty in obtaining accurate NMOC measurements, the U.S. Environmental Protection Agency (EPA) has provided monitoring and analytical assistance to these states through Radian Corporation. This assistance began in 1984 and continues through the 1990 NMOC Monitoring Program.

Between June 4 and September 28, 1990, Radian analyzed 593 ambient air samples, including 59 duplicate samples, collected in SUMMA® polished stainless steel canisters at 7 sites. These NMOC analyses were performed by the cryogenic preconcentration, direct flame ionization detection (PDFID) method.¹ Based on the 1984 through 1989 studies, the method was shown to be precise, accurate, and cost effective relative to the capillary column gas chromatographic, flame ionization detection (GC/FID) method (see Appendix B). The 1990 study confirmed these findings and supported the conclusion that the PDFID method is the method of choice to measure NMOC concentration in ambient air.

In 1986 specific toxic compounds, primarily aromatics and halocarbons, were also determined in the ambient air samples used for the NMOC analyses. In 1987 Radian Corporation developed a gas chromatographic multidetector (GC/MD) method to determine the concentration of 38 selected toxic organic compounds in ambient air. In 1988, air toxic analyses were conducted by GC/MD on ambient air samples taken at 13 of the 45 sites at which NMOC samples were taken. In 1989, air toxic analyses were conducted on ambient air samples taken at seven of the 23 sites at which NMOC samples were taken. In 1990, air toxic analyses were conducted on ambient air samples taken at three sites at which NMOC samples were taken. These samples were called 3-hour air toxics samples because the sampling period was three hours, from 6:00 a.m. to 9:00 a.m. A related monitoring program, the 1990 Urban Air Toxics Monitoring Program (UATMP), began sampling in March 1990 at urban sites and extended through February 1991. The samples from the latter program were 24-hour integrated ambient air samples and are referred to as UATMP samples throughout

this report. The final report for the 1990 UATMP will be presented under separate cover.

The Final Report for the 1990 Nonmethane Organic Compound and Three-Hour Air Toxics Monitoring program are included in Sections 1.0 through 12.0. Sections 1.0 through 6.0 report the data, procedures, and assessment of the NMOC portion of the monitoring program. Sections 7.0 through 10.0 report the data, procedures, and assessment of the 3-hour air toxics portion of the monitoring program. Section 11.0 lists references.

The sampling sites for the 1990 NMOC Monitoring Program are listed in Appendix A. Appendix A also gives the EPA Regions for each site, the Radian Site Code, the Aerometric Information Retrieval System (AIRS) site code and site information, and whether or not 3-hour air toxics analyses were performed on selected ambient air samples from the site.

Appendix B contains the detailed instructions on the Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID) method. Appendix C lists the 1990 NMOC Monitoring Program Site Data. Appendix D lists the 1990 NMOC Monitoring Program Invalidated and Missing Samples information. Appendix E gives PDFID Integrator Programming Instructions. Appendix F gives 1990 NMOC Daily Calibration Data. Appendix G gives 1990 In-House Quality Control Samples, and Appendix H gives Multiple Detector Speciated Three-Hour Site Data Summaries.

1.1 NMOC MONITORING PROGRAM

1.1.1 Introduction and Data Summary

The sampling schedule is given in the 1990 NMOC Quality Assurance Project Plan.² For all the sites in the 1990 NMOC Monitoring Program, sampling occurred from 6:00 a.m. to 9:00 a.m., Monday through Friday from June 4, 1990 through September 28, 1990. Table 1-1 gives details of the sample completeness results. Percent completeness, a quality measure is shown in Table 1-1. Completeness, which ratios the number of valid samples to the number of scheduled samples, averaged 95.8% in 1990 compared to 95.5% in 1989, 93.4% in 1988, 95.0% in 1987, 96.8% in 1986, 95.8% in 1985, and 90.6% in 1984. Percent completeness for 1990 ranged from 92.2 at HTCT to 100.00 for PLNJ. Statistics for the NMOC concentrations in parts per million carbon (ppmC) by volume are listed in Table 1-2. All sites collected samples from 6:00 a.m. to 9:00 a.m. Statistics in Table 1-2 include all duplicate sample concentrations.

TABLE 1-1. 1990 NMOC COMPLETENESS RESULTS

Radian Site Code	Scheduled Sampling Days	Total Scheduled Duplicate Samples	Total Scheduled Samples	Total Valid Duplicate Samples	Total Valid Samples	Percent Complete
BMTX	84	8	92	8	83	96.74
BRLA	74	7	81	9	77	95.06
HTCT	84	8	92	8	85	92.24
LINY	83	8	91	8	86	94.51
MNY	77	8	85	6	81	95.29
NWNJ	84	8	92	11	90	97.83
PLNJ	<u>84</u>	<u>8</u>	<u>91</u>	<u>9</u>	<u>91</u>	<u>100.00</u>
OVERALL	570	55	625	59	593	95.84

TABLE 1-2. 1990 NMOC SITE STATISTICS

Radian Site Code	No. of Samples	NMOC, ppmC						
		Minimum	Median	Mean	Maximum	Standard Deviation	Skewness	Kurtosis
<u>Sampling 6:00 to 9:00 a.m., local time</u>								
BMTX	83	0.558	1.440	1.717	4.283	0.901	1.213	0.733
BRLA	77	0.055	0.738	1.062	14.255	1.742	6.560	46.953
HTCT	85	0.066	0.205	0.257	0.738	0.145	1.253	1.239
LINY	86	0.060	0.298	0.409	1.867	0.353	2.087	4.915
MNY	81	0.186	0.502	0.803	6.200	0.888	4.012	19.113
NWNJ	90	0.110	0.381	0.464	2.040	0.284	2.418	10.155
PLNJ	<u>91</u>	<u>0.012</u>	<u>0.319</u>	<u>0.478</u>	<u>2.374</u>	<u>0.441</u>	<u>2.044</u>	<u>4.743</u>
Overall	593	0.012	0.726	0.727	14.255	0.940	6.837	82.333

1.1.2 Calibration and Drift

Each Radian PDFID channel was calibrated daily, using propane standards referenced to the National Institute of Science and Technology (NIST) Reference Material No. 1666B propane. Daily, before zero and calibration checks were performed, the analytical systems were purged with cleaned, dried air that had been humidified. Zero readings were determined with cleaned, dried air. Daily percent drift of the calibration factor ranged from -13.4% to +5.2 percent. The absolute value of the percent drift of the daily calibration factors ranged from zero to 13.4 percent.

1.1.3 NMOC Precision

Analytical precision was determined by repeated analyses of 22 site samples. Percent differences between the second and the first analysis averaged -1.36 percent. The average of the absolute values of the percent difference was 7.6% with a standard deviation of 10.3 ppmC. The analytical precision includes the variability between Radian channels and within Radian channels. The data quality objective for this measurement as published in the 1990 Quality Assurance Project Plan (QAPP)² was 9.8%, based on previous NMOC program experience³ with this measurement.

Overall precision, including sampling and analysis variability, was determined by analysis of 59 duplicate site samples, simultaneously collected in two canisters from a common sampling system. Percent difference for Radian's analyses of the duplicates averaged 6.33 percent. The average absolute percent difference was 12.3% with a standard deviation of 14.4 ppmC. The data quality objective for this measurement was 12.2%, based on previous experience.²

1.1.4 Accuracy

Because the NMOC measurements encompass a range of mixtures of unknown compounds, it was not possible to define absolute accuracy. Instead, accuracy was determined relative to propane standards with internal and external audit samples.

Accuracy was monitored internally throughout the program by the use of in-house propane standards. Periodically an in-house propane quality control

(QC) sample was prepared with a flow dilution apparatus and analyzed by the PDFID method. The propane used to prepare the in-house QC standards was certified by the EPA Quality Assurance Division (QAD) and was referenced to NIST propane Certified Reference Material (CRM) No. 1666B.

Figures 1-1 through 1-4 show the in-house quality control results for Radian Channels A, B, C, and D. Measured propane values are plotted against calculated propane standards. Table 1-3 shows the linear regression parameters for the Radian in-house quality control data. Quality control samples of propane were mixed from a propane standard certified by EPA-QAD and referenced to NIST propane Certified Reference Material (CRM) 1666B. The regression used the propane concentration calculated from the mixing operation as the independent variable and concentration measured by each Radian channel as the dependent variable. The concentration range of the in-house quality control samples was 0.159 to 1.464 ppmC. Table 1-3 indicates excellent quality control for each channel since, as expected, the intercepts are all near zero, and the slopes and coefficients of correlation are all near 1.0.

External propane audit samples were provided by EPA-QAD. The propane samples were referenced to NIST propane Certified Reference Material (CRM) 666B. Table 1-4 summarizes the percent bias of the Radian channels relative to the EPA-QAD channel. The audit samples were given Radian ID Numbers upon receipt. The average percent bias for the Radian channels was 1.07%, ranging from -3.18% for Channel D to +6.23% for Channel A. Absolute percent biases are listed in Table 1-5 and range from 2.19% for Channel C to 6.96% for Channel D, averaging 5.04% overall for the Radian channels.

1.1.5 Other Quality Assurance Measurements

The results of other quality assurance measurements are discussed below. Canister cleanup studies established that there was little carryover of NMOC from one sample to the next, using the canister cleanup apparatus and procedure developed for this study. In over 100 separate determinations, percent cleanup averaged 99.747 percent. Cleanup was defined in terms of the percent of the NMOC concentration that was removed in the cleanup cycle. Figure 1-5 shows a between-laboratory comparison of site sample analyses involving Radian channels and EPA-QAD channel for the PDFID method. Table 1-6 gives the orthogonal regression parameters, assuming a linear relationship,

IN-HOUSE PROPANE QC RESULTS

Channel A

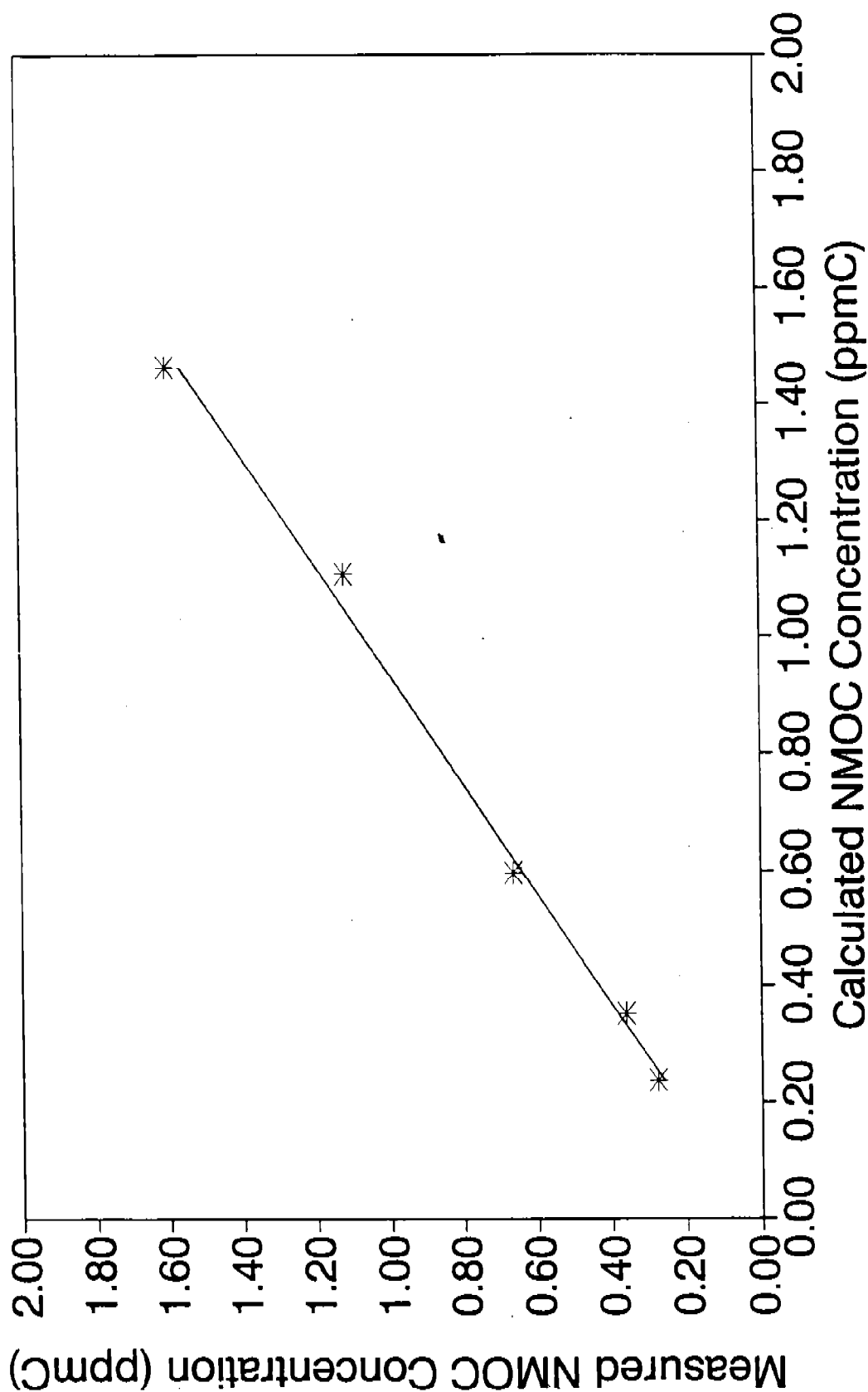


Figure 1-1 . In-house quality control results, Channel A .

IN-HOUSE PROPANE QC RESULTS

Channel B

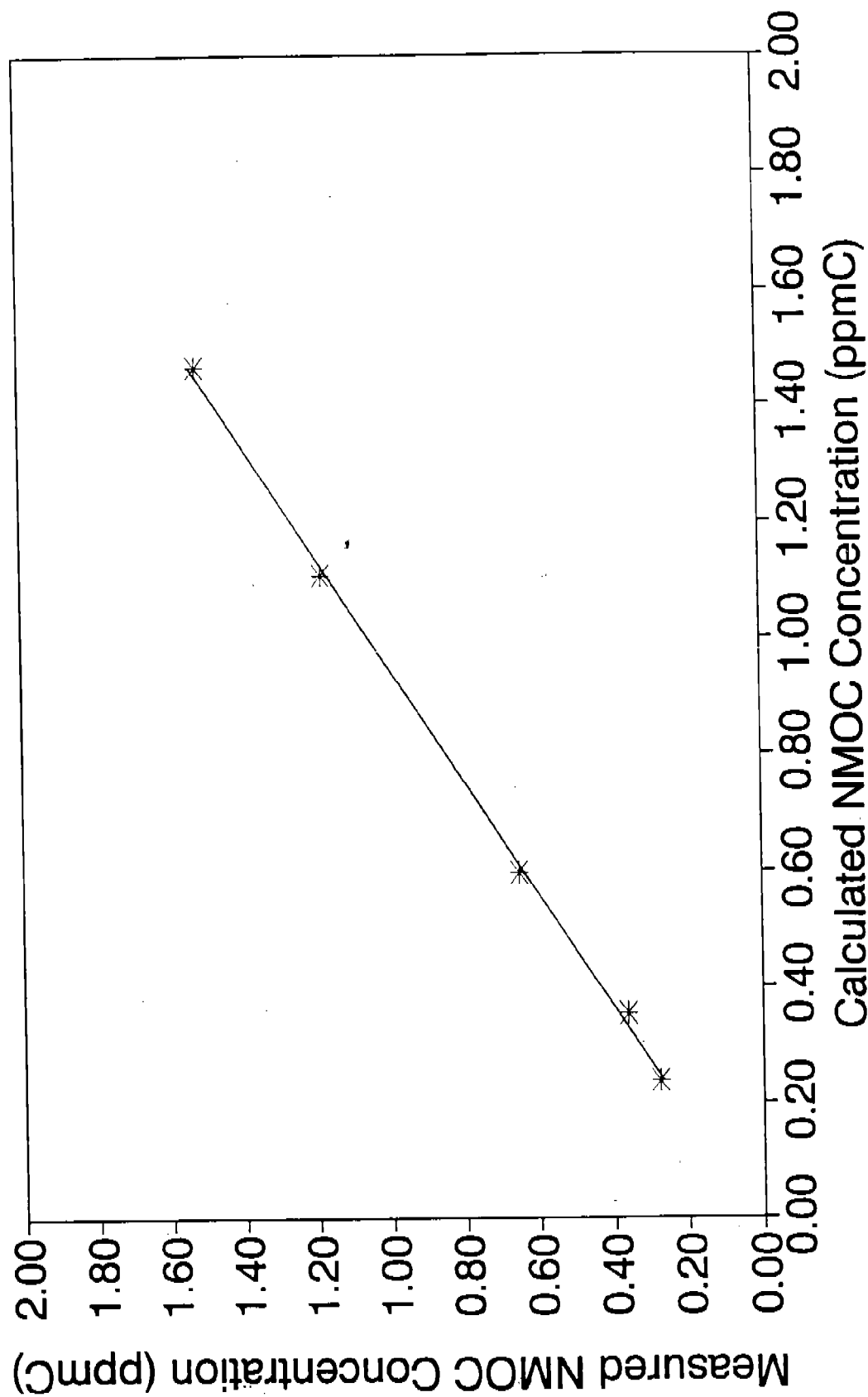


Figure 1-2. In-house quality control results, Channel B.

IN-HOUSE PROPANE QC RESULTS

Channel C

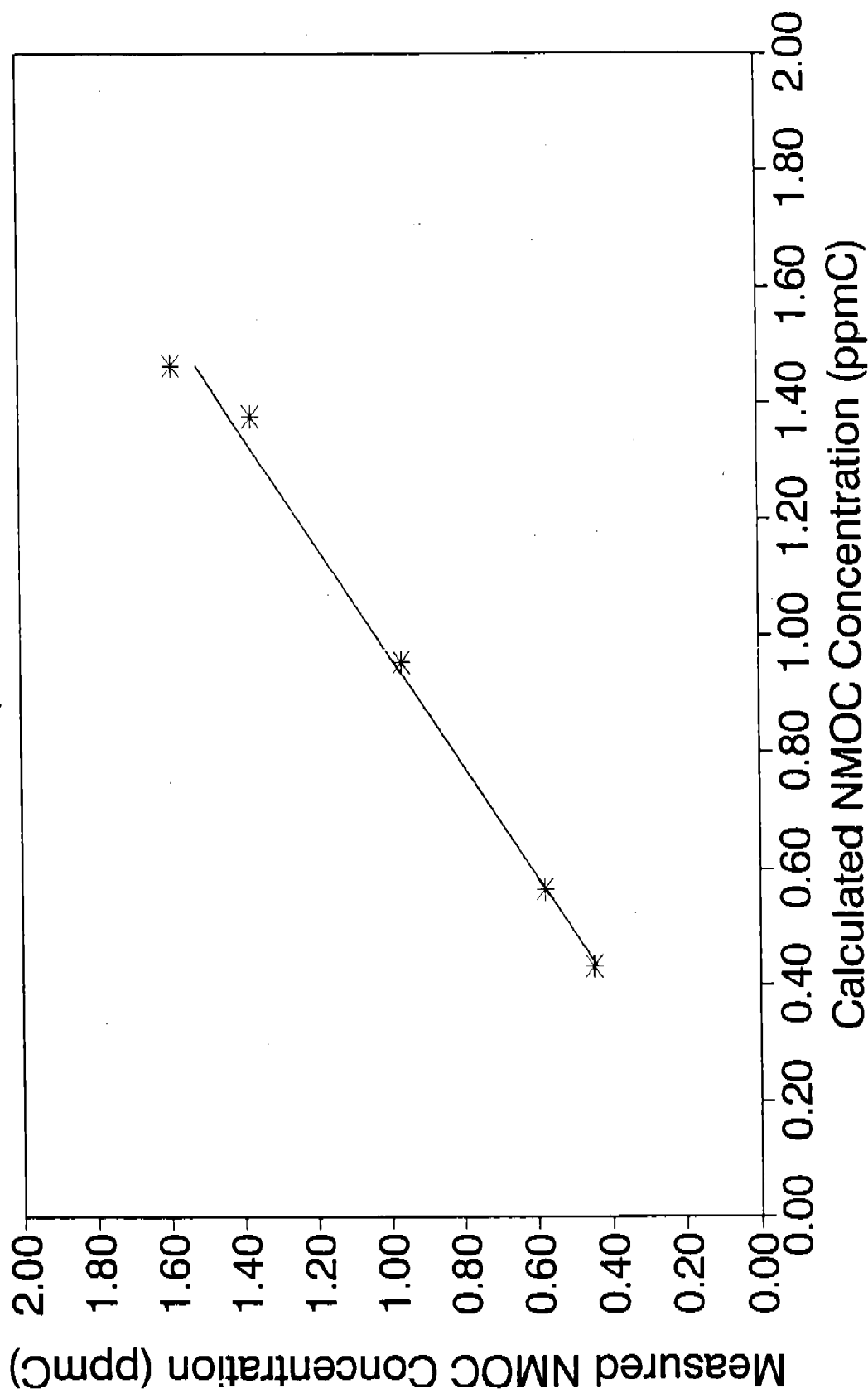


Figure 1-3. In-house quality control results, Channel C.

IN-HOUSE PROPANE QC RESULTS

Channel D

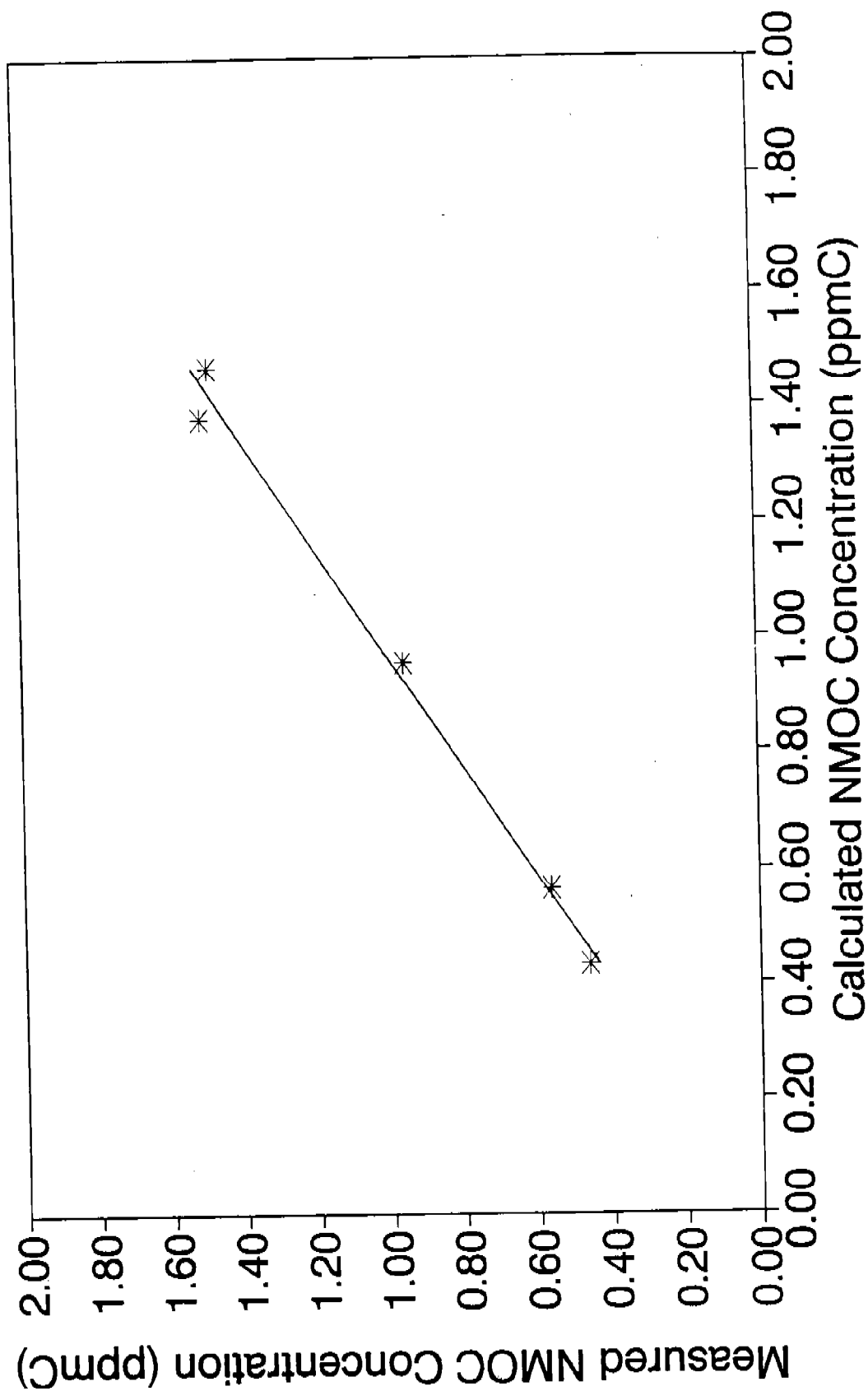


Figure 1-4. In-house quality control results, Channel D.

TABLE 1-3. LINEAR REGRESSION PARAMETERS FOR
IN-HOUSE QUALITY CONTROL DATA

Radian Channel	Cases	Intercept	Slope	Coefficient of Correlation
A	5	0.008606	1.060236	0.997253
B	5	0.025200	1.030042	0.999370
C	5	-0.014900	1.048497	0.995747
D	5	-0.017800	1.053398	0.995685

TABLE 1-4. AUDIT SAMPLE RESULTS, PERCENT BIAS^a

Radian ID Number	Channels				Radian Percent Bias
	A Percent Bias	B Percent Bias	C Percent Bias	D Percent Bias	
1053	2.19	-1.36	-0.39	-4.65	
1054	7.16	4.06	2.78	4.17	
1073	10.51	4.79	4.79	3.40	
1074	5.06	-8.93	-0.82	-15.62	
Average	6.23	-0.36	1.59	-3.18	1.07
Std. Dev.	3.50	6.34	2.67	9.21	6.01

^aPercent Bias = [(Measured NMOC - QAD NMOC) / QAD NMOC] x 100.

TABLE 1-5. AUDIT SAMPLE RESULTS, ABSOLUTE PERCENT BIAS^a

Radian ID Number	Channels				Radian Absolute Percent Bias
	A Percent Bias	B Percent Bias	C Percent Bias	D Percent Bias	
1053	2.19	1.36	0.39	4.65	
1054	7.16	4.06	2.78	4.17	
1073	10.51	4.79	4.79	3.40	
1074	5.06	8.93	0.82	15.62	
Average	6.23	4.78	2.19	6.96	5.04
Std. Dev.	3.50	3.13	2.02	5.80	3.87

^aAbsolute Percent Bias = $\text{ABS}[(\text{Measured NMOC} - \text{QAD NMOC}) / \text{QAD NMOC}] * 100$

1990 NMOC Program

Orthogonal Regression

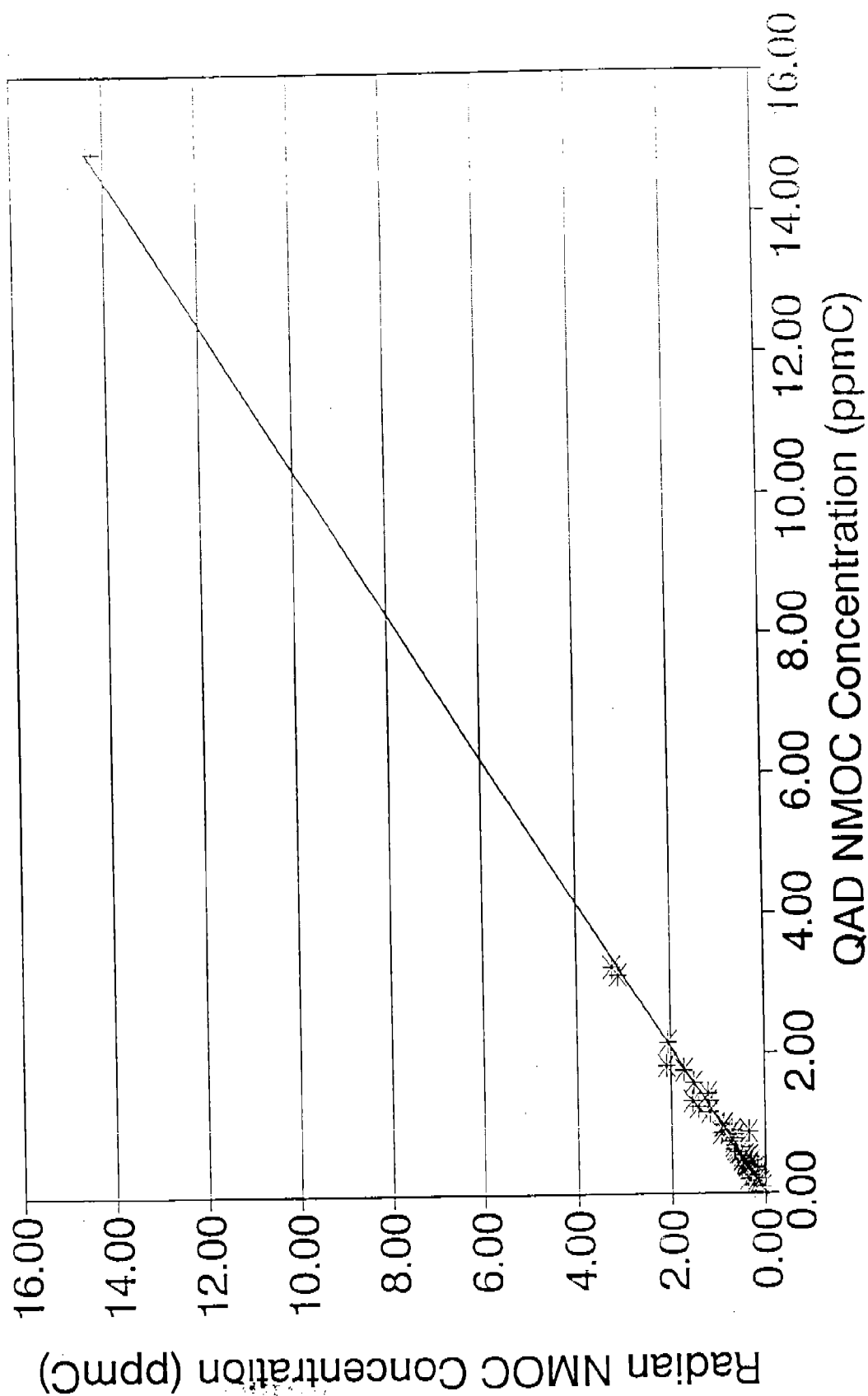


Figure 1-5. Orthogonal regression comparing QAD with Radian NMOC analyses.

TABLE 1-6. ORTHOGONAL REGRESSION PARAMETERS FOR COMPARATIVE
ANALYSES OF SITE SAMPLES

Channel Pair (X-Y)	Cases	Intercept	Slope	Coefficient of Correlation
QAD-Radian	202	-0.038190	1.025019	0.995887
Radian-QAD	202	0.037260	0.975590	0.995887

for Figure 1-5 and the other possible comparison. The type of orthogonal regression used here refers to a linear regression in which the Sum of Squares of the perpendicular distances between the data points and the regression line are minimized.

The results show good agreement because the intercepts are very close to zero, the slopes are within 3% of unity, and the coefficients of correlation are within 0.4% of unity. One hundred percent (100%) of the NMOC data base was validated by checking data transcriptions from original data sheets for 36 entries per sample. The errors found equal a data base error rate of 0.956 percent. The data validation included 100% of the reported NMOC concentration values. All errors that were found were corrected.

1.2 THREE-HOUR AIR TOXICS MONITORING PROGRAM

At three sites, Baton Rouge, LA (BRLA); Newark, NJ (NWNJ); and Plainfield, NJ (PLNJ), 3-hour NMOC samples were speciated by a GC/MD analytical system for 38 UATMP target compounds for a total of 25 NMOC ambient air samples. After NMOC analysis, the NMOC sample canisters were bled to atmospheric pressure, stored at least 18 hours for equilibration, and then analyzed by GC/MD. Duplicate samples were collected at all three of the sites simultaneously and analyzed individually by GC/MD. Replicate analyses were performed on one duplicate sample per site. A total of 31 GC/MD analyses were performed, including duplicate samples and replicate analyses.

1.2.1 Overall Data Summary

Twenty-six target compounds were identified in the 31 analyses. Benzene, m/p-xylene, toluene, ethylbenzene, styrene/o-xylene, carbon tetrachloride, and 1,1,1-trichloroethane were the most frequently identified compounds. Concentrations of the target compounds identified ranged from 0.004 ppbv for n-octane to 20.60 ppbv for propylene. The overall average concentration of the target compounds identified was 1.63 ppbv, averaged over all sites and target compounds. The air toxics data are tabulated by site code in Section 7 (Table 7-4) showing numbers of cases identified, minima, maxima, and means for all target compounds.

1.2.2 Site Results

Overall site mean concentrations were 2.34 ppbv for BRLA, 1.34 ppbv for NWNJ, and 1.12 ppbv for PLNJ averaged over all target compounds identified. These air toxic data are presented in Section 7.0.

1.2.3 Gas Chromatography/Mass Spectrometry Confirmation Results

Three 3-hour air toxics ambient air samples representing 10% of the total samples were analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for compound identification confirmation of the GC/MD analyses. The GC/MS analyses were performed after the GC/MD analyses. The GC/MS analyses confirmed 88.57% of the GC/MD analyses.

For the 3-hour air toxics samples the negative GC/MD-positive GC/MS analyses were 9.52 percent. The positive GC/MD-negative GC/MS analyses were 1.90 percent. Comparisons labeled "negative GC/MD-positive GC/MS" refer to specific samples in which a compound was not identified by GC/MD but positively identified by GC/MS analysis. Comparisons labeled "positive GC/MD-negative GC/MS" indicate specific samples in which a compound was positively identified by GC/MD but not identified by GC/MS analysis.

1.2.4 Precision

Sampling and analytical precision of 3-hour air toxics samples was estimated by analyzing duplicate samples. In terms of overall average absolute percent difference, the sampling and analysis precision was 38.40 percent.

Analytical precision was estimated by repeated analyses of three duplicate samples. The analytical precision measured by the overall average absolute percent difference was 3.40 percent. Both the sampling and analytical precision results are excellent in view of the concentration range found in this study.

The data analyses showed that both for the duplicate and replicate results, the imprecision was significantly higher at concentrations less than 2 ppbv. Both the duplicate sample and repeated analyses results are discussed in Section 8.0.

1.2.5 External Audit

The external audit for the 3-hour air toxics compounds is conducted bimonthly on the Urban Air Toxics Program and the results will be reported in the 1990 UATMP Final Report. The audit samples that are used are furnished by the Quality Assurance Division of the U.S. EPA.

2.0 NMOC DATA SUMMARY

This section presents the data summary for the 1990 NMOC Monitoring Program conducted during June, July, August, and September. Daily NMOC concentrations and other pertinent monitoring data are given by site in Appendix C. The majority of the data presented in this section summarize the NMOC concentrations measured for samples collected at seven sites throughout the continental United States. Sites were selected in urban and/or industrial locations; they are described in Appendix A. The site codes for the 1990 NMOC Monitoring Program are listed in Appendix A and are used throughout the report to identify the sites. Samples were collected in 6-liter (L) stainless steel canisters by local site operators trained by Radian Corporation personnel. The sampling procedure was described in detailed written instructions and given to the site operators. The sampling procedure instructions also appear in Section 3.1.2. Analytical concentration measurements of NMOC were made in the Radian Corporation Research Triangle Park (North Carolina) laboratory according to the PDFID method TO-12.¹ The complete procedure is described in Appendix B.

The concentration of oxides of nitrogen (NO_x), site temperature, barometric pressure, wind direction, and weather conditions were provided on the field sampling forms by site personnel at the time of sampling. These data were recorded in the 1990 NMOC data base, but are not presented in this report because they were not measured by Radian equipment or personnel, nor were the data subjected to project quality assurance procedures.

Table 2-1 lists the NMOC Monitoring Program completeness results by site code. The scheduling of sample days and the scheduling of duplicate analyses is given in the QAPP.² For the 1990 NMOC sites, completeness was over 90%, and generally very near to 100 percent. A complete listing of invalid samples and the reasons for the invalidation are given in Appendix D.

Overall completeness figures for the 1990 NMOC Program show 95.8% complete. This compares with 95.5% in 1989, 93.4% in 1988, 95.0% complete in 1987, 96.8% complete in 1986, 95.8% complete in 1985 and 90.6% complete in 1984.^{3,4,5,6,7,8}

TABLE 2-1. 1990 NMOC COMPLETENESS RESULTS

Radian Site Code	Scheduled Sampling Days	Total Scheduled Duplicate Samples	Total Scheduled Samples	Total Valid Duplicate Samples	Total Valid Samples	Percent Complete
BMTX	84	8	92	8	83	96.74
BRLA	74	7	81	9	77	95.06
HTCT	84	8	92	8	85	92.24
LINY	83	8	91	8	86	94.51
MNY	77	8	85	6	81	95.29
NWNJ	84	8	92	11	90	97.83
PLNJ	<u>84</u>	<u>8</u>	<u>91</u>	<u>9</u>	<u>91</u>	<u>100.00</u>
OVERALL	570	55	625	59	593	95.84

Completeness was defined as the percentage of samples, scheduled in the QAPP,² that were collected and analyzed as valid samples, beginning with the first valid sample and ending with the last scheduled sample, with the exception of MNY. An unexpected site situation forced MNY to collect its last sample on September 20, 1990.

Table 2-2 summarizes statistics by sites. All sites collected an integrated sample from 6:00 a.m. to 9:00 a.m. The overall average of the NMOC concentration is seen to be 0.716 ppmC. The averages pertain only to the sites for the 1990 Monitoring Program.

In Table 2-2, the means are the arithmetic averages of the NMOC concentrations at each site. The numbers given for standard deviation, skewness, and kurtosis are the second, third, and fourth moments, respectively about the arithmetic means. A skewness value greater than zero applies to distributions having a longer tail to the right. A distribution that is normally distributed would have a kurtosis of 3.0. A distribution more peaked (or pointed) than a normal distribution, having the same variance, would have a kurtosis greater than 3.0. All the kurtosis figures listed in this report are zero centered, which means that 3.0 has been subtracted from the fourth moment to give a reported kurtosis of 0.0 for a symmetrical distribution.

NMOC monitoring data can be better characterized by a lognormal distribution than by a normal distribution, following the findings of previous years.^{3,4,5,6,7,8} Table 2-3 summarizes the 1990 NMOC data using the definitions that characterize a lognormal distribution overall and for each site. MU and SIGMA are the mean and standard deviation, respectively, of the logarithm of NMOC to the Napierian base e. The geometric mean is e raised to the power MU; the geometric standard deviation is e raised to the power SIGMA. The mode is the most frequently occurring logarithm of NMOC value for a continuous probability distribution function.

Information listed in Appendix A includes the location of the site, street address as well as the Universal Transverse Mercator (UTM) coordinates for the site, the site code used throughout this report, the Aerometric Information Retrieval System (AIRS) Number. Appendix A gives the AIRS printouts for all the sites that are in the system for 1990.

TABLE 2-2. 1990 NMOC SITE STATISTICS

Radian Site Code	NMOC, ppmC						
	Minimum	Median	Mean	Maximum	Standard Deviation	Skewness	Kurtosis
<u>Sampling 6:00 to 9:00 a.m., local time</u>							
BMTX	0.558	1.440	1.717	4.283	0.901	1.213	0.733
BRLA	0.055	0.738	1.062	14.255	1.742	6.560	46.953
HTCT	0.066	0.205	0.257	0.738	0.145	1.253	1.239
LINY	0.060	0.298	0.409	1.867	0.353	2.087	4.915
MNY	0.186	0.502	0.803	6.200	0.888	4.012	19.113
NWNJ	0.110	0.381	0.464	2.040	0.284	2.418	10.155
PLNJ	<u>0.012</u>	<u>0.319</u>	<u>0.478</u>	<u>2.374</u>	<u>0.441</u>	<u>2.044</u>	<u>4.743</u>
Overall	0.012	0.726	0.727	14.255	0.940	6.837	82.333

TABLE 2-3. 1990 NMOC LOGNORMAL STATISTICS

Radian Site Code	Parameters of the Lognormal Distribution of NMOC, ppmC					Parameters of Logarithmic Transformation of NMOC Concentrations	
	Minimum	Mode	Median	Mean ^a	Maximum	MU ^b	SIGMA ^c
<u>Sampling 6:00 to 9:00 a.m., local time</u>							
BMTX	0.558	1.199	1.440	1.715	4.283	0.420	0.489
BRLA	0.055	0.343	0.738	0.995	14.255	-0.360	0.843
HTCT	0.066	0.169	0.205	0.256	0.738	-1.500	0.528
LINY	0.060	0.172	0.298	0.407	1.867	-1.185	0.758
MNY	0.186	0.370	0.502	0.761	6.200	-0.514	0.694
NWNJ	0.110	0.296	0.381	0.463	2.040	-0.919	0.547
PLNJ	<u>0.012</u>	<u>0.152</u>	<u>0.319</u>	<u>0.497</u>	<u>2.374</u>	<u>-1.095</u>	<u>0.889</u>
Overall	0.012	0.206	0.726	0.711	14.255	-0.754	0.909

^aMean = $\exp (MU + SIGMA^2/2)$.

^bMU is the mean of $\ln(NMOC)$. e^{MU} is the geometric mean.

^cSIGMA is the standard deviation of $\ln(NMOC)$. e^{SIGMA} is called the geometric standard deviation.

Appendix C gives the daily NMOC concentration data listed chronologically for the entire sampling season. In addition, figures are given for each site in which NMOC concentrations in ppmC are plotted versus the 1990 Julian date on which the sample was taken. Data tables for each site include the following:

- calendar date sampled;
- Julian date samples;
- weekday sample (M, T, W, H, F);
- sample ID number, assigned consecutively upon receipt of the sample;
- sample canister number;
- Radian analysis channel;
- NMOC concentration in ppmC, determined by Radian; and
- NMOC concentration in ppmC, determined by U.S. EPA, Quality Assurance Division.

Appendix D lists invalidated or missing samples. Table D-1 lists these data chronologically, while Table D-2 groups the listings by site code. For each sample, the tables list the site code, the date of the missing or invalid sample, a brief description of the possible cause of the invalid or missing sample, and the assigned cause for the failure.

3.0 NMOC TECHNICAL NOTES

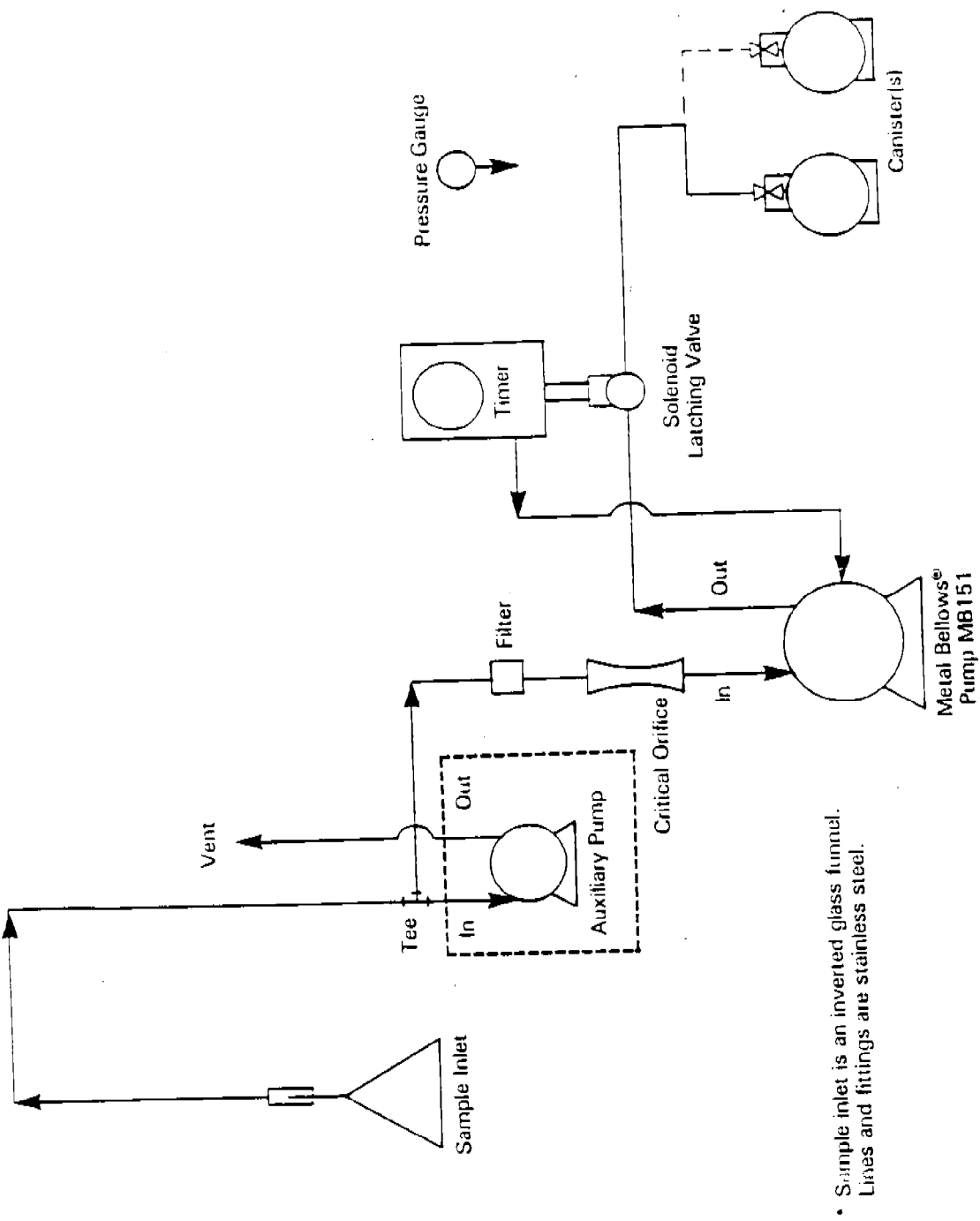
This section summarizes descriptions of the installation and operation of the field sampling equipment, a summary of the analytical equipment and procedures for NMOC measurement, and a description of the canister cleanup equipment and procedures.

3.1 NMOC FIELD SAMPLING EQUIPMENT

The field sampling equipment used to collect ambient air samples for NMOC measurement is relatively simple to operate. Ambient air is drawn through a sintered stainless steel filter (2 micron) and critical orifice by a Metal Bellows® pump and delivered to a SUMMA® canister. The sampler components are made of stainless steel. Figure 3-1 is a schematic diagram of the NMOC sampling system.

3.1.1 Installation

NMOC sampler installation configurations were site dependent. All field sites were installed by or under the direction of Radian personnel. Installation requirements included a temperature-controlled environment (70° to 86°F), close proximity to the atmosphere to be sampled, and noncontaminating sampler connections. Glass tubing or gas-chromatographic-grade stainless steel tubing and stainless steel fittings are the preferred materials of construction for all connections contacting the sample. Typical sampler installations involved three configurations including direct connections to a ventilated glass manifold, a slipstream connection prior to the station NO_x analyzer with a bypass pump, or collocated NMOC and NO_x sample inlet lines. For sites where the distance between the sample inlet and the stainless steel post was greater than eight feet, an auxiliary pump, as shown in Figure 3-1, was used. The auxiliary pump helps ensure that the air in the sample line is representative of the ambient air. The critical orifice was sized to maintain a constant flow rate and to fill a 6-L stainless steel canister from the 0.5 mm Hg vacuum to about 15 psig in three hours. When duplicate samples were taken, the critical orifice used for single sample collection was replaced with an orifice sized to fill two canisters during the 3-hour sampling period.



• Sample inlet is an inverted glass funnel.
Lines and fittings are stainless steel.

Figure 3-1. Sampling system for collecting 3-hour integrated ambient air samples.

3.1.2 Operation

Presampling

The following instructions pertain to the sampling operation prior to collection of the field sample.

1. Verify timer program (see timer instructions). Set to MANUAL position to leak check sampling system. Once the system passes the leak check, turn timer to AUTO position.
2. With no canisters connected to the sampling system, turn the timer switch to the MANUAL position.
3. Disconnect the sample inlet from the top of the orifice/filter assembly mounted on the pump inlet. Connect the rotameter to the top of the orifice/filter assembly. Tighten Swagelok® (1/4") fitting securely with a wrench. Do not overtighten.
4. Turn timer switch ON. Do not turn the power off and on rapidly. Wait 20 seconds between cycles to prevent premature timer/solenoid failure. The pump should run and the latching valve should open (audible click with 2 to 5 seconds delay). Verify that the rotameter reading is approximately the same ($\pm 15\%$) as the reading obtained during installation as recommended on the orifice tag. If the rotameter reading is not correct, see the troubleshooting instructions.
5. Allow the pump to run for at least 20 seconds, then press the timer OFF button.
6. Connect a cleaned, evacuated canister to the sampling system. If duplicate samples are to be collected, remove the plug from the second port of the tee and connect a second canister to the sampling system. Remove the orifice assembly marked with an "S," denoting a single orifice. Install the orifice assembly marked with a "D," denoting a double orifice. Replace the filter holder on the "D" orifice. After obtaining scheduled duplicate samples, replace the plug and the "S" orifice assembly to return to single sample collection status.
7. With the pump off, open completely the valve on the canister (or on one of the canisters if two are connected) and verify that no flow is registered on the rotameter. If any flow is detected by the rotameter, immediately close the canister valve and see the troubleshooting instructions.
8. If no flow is observed, disconnect the rotameter and reconnect the inlet sample line to the filter assembly. If two canisters are connected, completely open the valve on the second canister.

9. Reverify that the canister valve(s) is (are) completely open and the timer is properly set for sampling from 6 a.m. to 9 a.m. the next weekday. Set timer to AUTO mode.
10. Reset the elapsed time counter.

Postsampling

The instructions that follow outline the NMOC postsampling operation procedures in the field.

1. Close the canister valve(s) firmly. Disconnect the canister(s) from the sampling system.
2. Connect the pressure gauge to the canister inlet and open the canister valve. Record the canister pressure on the field sampling data form. Close the canister valve and remove the pressure gauge. Repeat pressure measurement for second canister if collecting a duplicate sample. If the pressure reading is not at least 11 psig, see the troubleshooting instructions.
3. Fill in the required information on the NMOC SAMPLING FIELD DATA FORM. PLEASE PRESS HARD AND WRITE WITH A BALLPOINT PEN; YOU ARE MAKING THREE COPIES. (see Figure 3-2).
4. Verify elapsed time counter reading equals 3 hours.
5. Verify that the timer shows the correct time setting. If not, note that fact on the sample form along with any information pertaining to the possible cause. Reset the timer to the correct time, if necessary.
6. Verify that the canister valves are closed firmly. Do not overtighten them. Put the protective cap(s) on the valve(s) and prepare the canister(s) for shipment to Radian, RTP.

3.1.3 Troubleshooting Instructions

A list of troubleshooting instructions was given to each field site during the site installation and operator training. Typical problems encountered with the field sampling apparatus included: loose fittings, misprogrammed timer, or clogged orifices. To minimize downtime, field site operators were encouraged to relay sampling problems to the Radian laboratory daily, by telephone. Most sampling problems were addressed promptly through these telephone discussions.

**NMOC SAMPLING FIELD DATA FORM**

Site Code : _____ SAROAD # : _____
Site Location : City: _____ State: _____
Sample Collection Date : _____ Sampling Period : _____
Operator : _____ Elapsed Time : _____
Final Canister Pressure (psig) : _____
Sample Canister Number : _____ Side : _____
Sample Duplicate for this Date : Yes ☐ No ☐
If yes, Duplicate Canister Number : _____
NOx Analyzer Operating? Yes ☐ No ☐
If yes, Average Reading (ppmv as NOx) : _____
Average Wind Speed : _____ Average Wind Direction : _____
Rotameter Indicated Flow Rate : _____ Orifice Number : _____
Average Barometric Pressure (mm Hg or inches Hg) : _____
Ambient Temperature (°F) : _____ Relative Humidity : _____
THC Model (if available) : _____ Average THC : _____
Sky/Weather Conditions : _____

Site Conditions/Remarks : _____

Canister Number : _____
Initial Canister Vacuum : _____

Received By : _____
Date : _____
Sample Validity : _____
If Invalid, Reason : _____

0781189R

Figure 3-2. NMOC Sampling field data form.

3.1.4 Sampler Performance for 1990

The NMOC sampler was modified in 1989 to improve performance. This modification involved replacing the mechanical timer previously used with an electronic version. The electronic timer improves sample integration. An elapsed time counter was added to the sampler to verify sample duration. This modified system was used during the 1990 program. In addition, all sampler orifice(s) and canisters were subjected to a preseason QC check to ensure field performance. All orifices were checked against the rotameter enclosed in each sampling kit, and referenced to a transfer standard (bubble flowmeter). Prior to field installation, all samplers were operated in the laboratory to establish an expected final pressure range for the canister samples. Two single orifices and one double orifice were tested for each sampler kit.

Due to the preseason checks and modifications, the NMOC sampler performance was improved for the 1990 sampling season. This assessment is based on the consistency of the final sample pressures on a site-specific basis (see Section 4.6). The sampler performance in terms of successful sample collection (i.e., completeness) was comparable to previous years. Overall completeness from all sites averaged 94.9 percent. The site-specific completeness ranged from 92.2% for BRLA to 100.0% for PLNJ.

Invalidated samples were primarily due to operator error and equipment problems. Completeness can be improved at all sites through greater attention to sampling procedure, and by ensuring that trained site personnel are available.

A total of 26 invalidated/missing samples were recorded in the 1990 NMOC Monitoring Program. Appendix D lists the invalidated/missing samples in chronological order. Also, the reason for invalidation is presented. Avoidable operator error accounts for 69% and equipment problems account for 27% of the invalidated samples. The remaining 4% reflects one missed sample collection.

A further improvement in completeness may be possible as site operators gain familiarity with the electronic timer. Revised sampler operating instructions will focus additional attention on timer programming

and operation, and will include a daily checklist to eliminate common operator errors.

3.1.5 Field Documentation

The field sample collection information was documented by the site operator on printed forms. Figure 3-2 is an example NMOC Sampling Field Data Form. Each canister sent to the field was accompanied by this form. The field data form is a multiple part unit. A copy of the field data form was retained by the site operator for the site notebook. Figure 3-3 is the Invalid Sample Form. This form was completed by the site operator to document the reasons for a missed or invalid field sample collections.

3.2 NMOC ANALYSIS

The NMOC analysis equipment and analysis procedure are described in greater detail in Appendix B. A brief description of the equipment and operating procedure used in this study follows.

3.2.1 Instrumentation

Two gas chromatographs were used by Radian. Each was a dual-channel Hewlett-Packard Model 5880 (HP-5880) using flame ionization detection (FID). NMOC instrument Channels A and B refer to the two FIDs on one HP-5880 unit, and Channels C and D refer to the two FIDs on the other HP-5880 unit. These chromatographs were modified to be similar to the prototype unit (EPA-QAD instrument), which is described in Appendix B. The EPA-QAD instrument was used as a reference during this program.

3.2.2 Hewlett-Packard, Model 5880, Gas Chromatograph Operating Conditions

The sample trap consisted of 30 cm of 1/8-inch outside diameter (o.d.) stainless steel tubing, packed with 60/80 mesh glass beads.

Three support gases were used in this analysis: helium, hydrogen, and hydrocarbon-free air. Details of their use are given in Table 3-1.

The operating temperatures of the HP-5880 were controlled for the NMOC analysis. The FID and auxiliary area were controlled at 250°C and 90°C, respectively. The oven temperature was programmed from 30°C to 90°C at a rate of 30°C per minute for 4 minutes, holding at 90°C for the fourth minute. Oven and integration parameters were controlled by HP Level 4 programmable integrators. A complete listing of the integrator programming sequence for NMOC measurement by the PDFID method is given in Appendix E.

NMOC INVALID SAMPLE FORM

Site Code : _____ SAROAD # : _____

City : _____ State : _____

Sample Collection Date : _____ Operator : _____

Sample Canister Number : _____

Sample Duplicate for this Date : Yes ☐ No ☐

If Yes, Duplicate Canister Number : _____

Reason for Invalid or Missed Sample : _____

Average NOx Analyzer Reading for this Collection Date : _____

Wind Speed : _____ Wind Direction : _____

Average Barometric Pressure (mm Hg or inches Hg) : _____

Ambient Temperature (°F) : _____ Relative Humidity : _____

Sky/Weather Conditions : _____

Received By : _____

Date : _____

Action Taken : _____

Resolution : _____

Field Invalid or In-house Invalid

Figure 3-3. NMOC Invalid sample form.

TABLE 3-1. SUPPORT GAS OPERATING CONDITIONS

Purpose	Cylinder Composition	Pressure	Mean Flow Rate ^a
Carrier Gas	Helium	30 psig	29.5 mL/min
FID Air	Hydrocarbon- free air	30 psig	300.7 mL/min
FID Fuel	Hydrogen	32 psig	29.0 mL/min

^aFlow rates corrected to standard conditions (1 atmosphere pressure, 20°C).

3.2.3 NMOC Analytical Technique

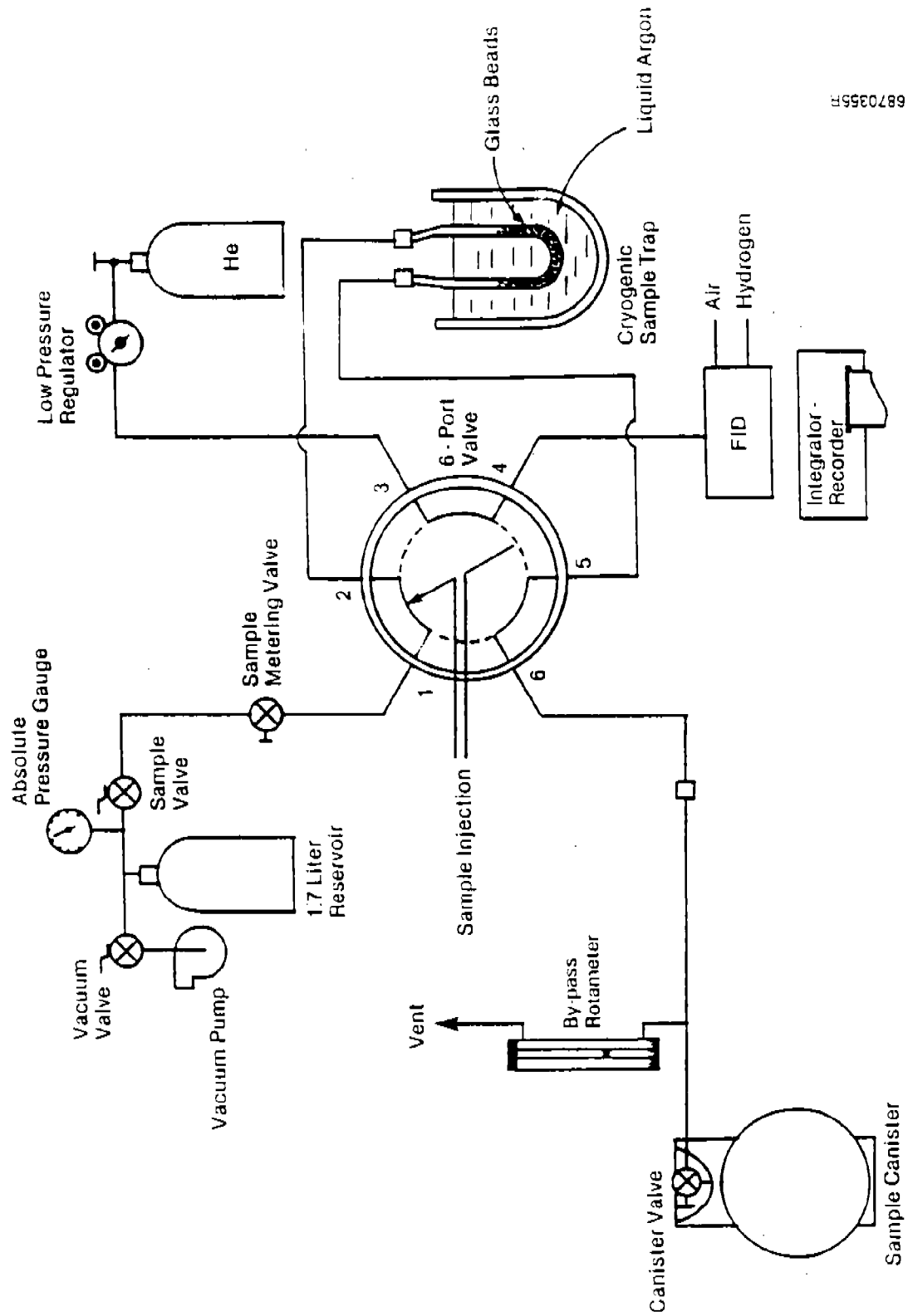
The modified HP-5880, dual-FID chromatographs were operated during the 1990 study according to a project specific Standard Operating Procedure (SOP). Further description is given below to help explain the analytical apparatus and procedure.

The six-port valve shown in Figure 3-4 was installed in the auxiliary heated zone of the HP-5880 and was pneumatically actuated using chromatographic valve control signals to apply either compressed air or vacuum to the valve. The sample trap itself was located inside the chromatograph's column oven. A section of 1/16-inch o.d. stainless steel tubing was sized to a length that prevented pressure and flow surges from extinguishing the FID flame. This length was determined experimentally and differs for each chromatograph and for each channel within chromatographs. Although the length of tubing effectively substitutes for the pressure restriction provided by a column, it does not perform the separation function of a column.

During sample trapping, a slight excess of sample gas flow was maintained. A pressure change of 80 mm Hg in a 1.7-L vacuum reservoir was used to gauge and control the volume of sample gas cryogenically trapped. After the trapping cycle was complete, the HP-5880 program shown in Appendix B was initiated. When the program triggered a horn emitting an audible beep, the cryogen was removed from the trap and the oven door was closed. The chromatographic program then assumed control of raising the oven temperature, at the preset rate, to release the trapped sample to the FID, and set up the integration parameters.

3.3 CANISTER CLEANUP SYSTEM

A cleanup cycle consisted of first pulling a vacuum of 0.5 mm Hg absolute pressure in the canister, followed by pressurizing the canister to 20 psig with cleaned, dried air that had been humidified. This cycle was repeated two more times during the canister cleanup procedure. The cleanness of the canister was qualified by PDFID analysis. Upon meeting the cleanness criterion, the canister was evacuated to 0.5 mm Hg absolute pressure a fourth time, in preparation for shipment to the site.



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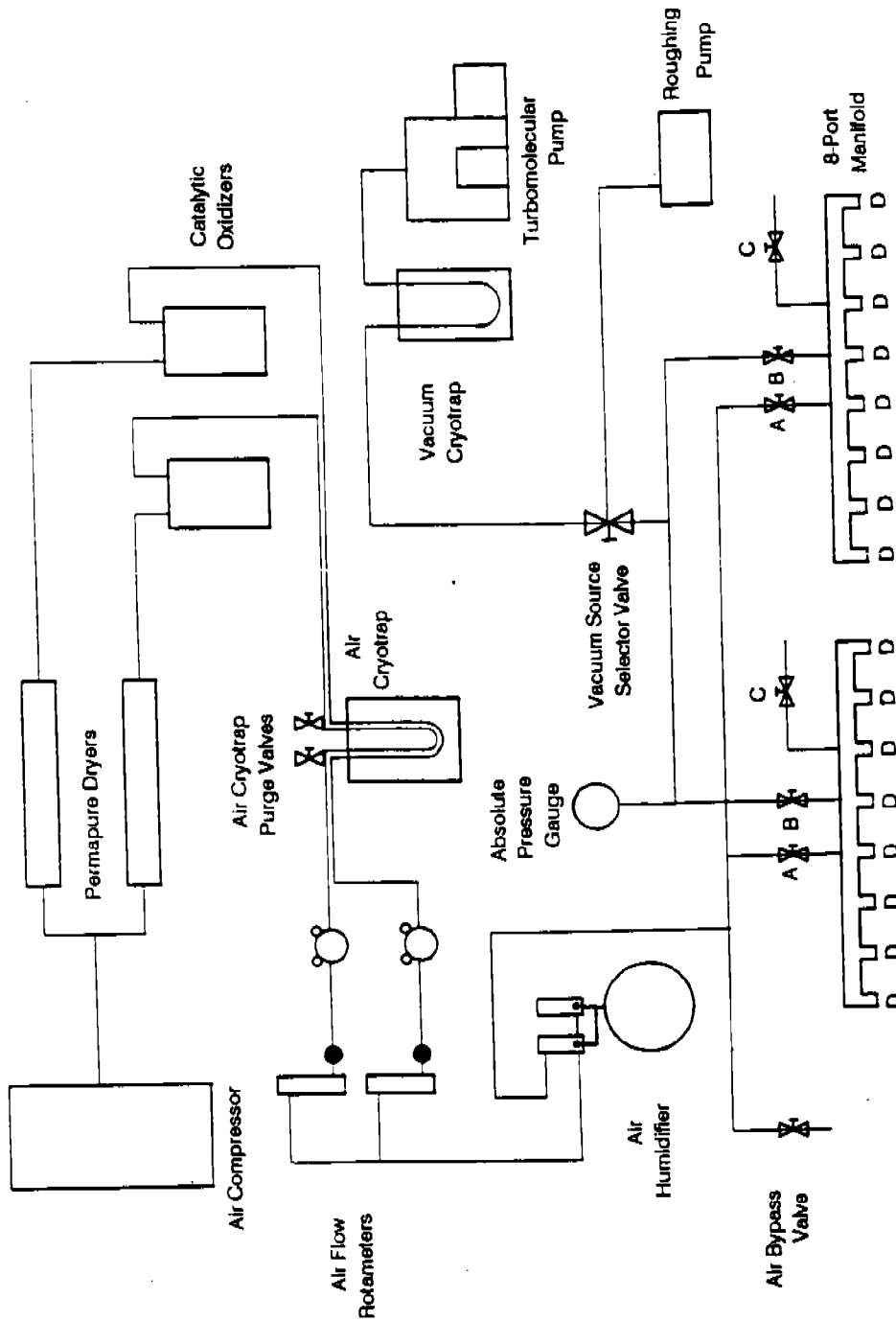
Figure 3-4. NMOG analytical equipment.

3.3.1 Canister Cleanup Equipment

A canister cleanup system was developed and used to prepare sample canisters for reuse after analysis. A diagram of the system is shown in Figure 3-5. An oil-free compressor with a 12-gallon reservoir provided source air for the system. The oil-free compressor was chosen to minimize hydrocarbon contamination. The compressor reservoir was drained of condensed water each morning. A coalescing filter provided water mist and particulate matter removal down to a particle size of one micron. Permeation dryers removed water vapor from the compressor source air. These permeation dryers were followed by moisture indicators to show detectable moisture in the air leaving the dryer. The moisture indicators never showed any water, indicating that the permeation dryers effectively removed all of the water vapor.

Air was then passed through catalytic oxidizers to destroy residual hydrocarbons. The oxidizers were followed by inline filters for secondary particulate matter removal, and by a cryogenic trap to condense any water formed in the catalytic oxidizers and any organic compound not destroyed by the catalytic oxidizer. A single-stage regulator controlled the final air pressure in the canisters and a metering valve was used to control the flow rate at which the canisters were filled during the cleanup cycle. The flow was indicated with a rotameter installed in the clean, dried air line. There was a shutoff valve between the rotameters and the humidifier system. The humidifier system consisted of a SUMMA® treated 6-L canister partially filled with high performance liquid chromatographic-grade (HPLC-grade) water. One flowmeter and flow-control valve routed the cleaned, dried air into the 6-L canister where it was bubbled through the HPLC-grade water. A second flow-control valve and flowmeter allowed air to bypass the canister/bubbler. By setting the flow-control valves separately, the downstream relative humidity was regulated. For the 1990 study, 80% relative humidity was used for canister cleaning. There was another shutoff valve between the humidifier and the 8-port manifold where the canisters were connected for cleanup.

The vacuum system consisted of a Precision Model DD-310 turbomolecular vacuum pump, a cryogenic trap, an absolute pressure gauge, and a bellows valve connected as shown in Figure 3-5. The cryogenic trap prevented the sample



- A. Manifold Air Pressure Valve
- B. Manifold Vacuum Valve
- C. Manifold Pressure Release Valve
- D. Manifold Port for Connecting Canisters to be Cleaned

Figure 3-5. Canister cleanup apparatus.

canisters from being contaminated by back diffusion of hydrocarbons from the vacuum pump into the cleanup system. There are no oil-free high vacuum pumps currently available at a competitive cost. The bellows valves enabled isolation of the vacuum pump from the system without shutting off the vacuum pump.

3.3.2 Canister Cleanup Procedures

After NMOC analyses were completed, a bank of eight canisters was connected to each manifold shown in Figure 3-5. The valve on each canister was opened, with the shutoff valves and the bellows valves closed. The vacuum pump was started and one of the bellows valves was opened, drawing a vacuum on the canisters connected to the corresponding manifold. After reaching 0.5 mm Hg absolute pressure as indicated by the absolute pressure gauge, the vacuum was maintained for 30 minutes on the eight canisters connected to the manifold. The bellows valve was then closed and the cleaned, dried air that had been humidified was introduced into the evacuated canisters until the pressure reached 20 psig. The canisters were filled from the clean air system at the rate of 7.0 L/min. This flow rate was recommended by the manufacturer as the highest flow rate at which the catalytic oxidizers could handle elimination of hydrocarbons with a minimum 99.7% efficiency.

When the first manifold had completed the evacuation phase and was being pressurized, the second manifold was then subjected to vacuum by opening its bellows valve. After 30 minutes, the second manifold was isolated from the vacuum and connected to the clean, dried air that had been humidified. The first manifold of canisters was then taken through a second cycle of evacuation and pressurization. Each manifold bank of eight canisters was subjected to three cleanup cycles.

During the third cleanup cycle, the canisters were pressurized to 20 psig with clean, dried air that had been humidified. For each bank of eight canisters, the canister having the highest precleanup NMOC concentration was selected for NMOC analysis to determine potential hydrocarbon residues. If the analysis measured less than 0.020 ppmC, then the eight canisters on the manifold were considered to be clean. Finally the canisters were again evacuated to 0.5 mm Hg pressure absolute; they were capped under vacuum and then packed in the containers used for shipping to the field sites.

4.0 NMOC QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

This section details the steps taken in the 1990 NMOC Monitoring Program to ensure that the data taken were of known quality and were well documented. Analysis results are given in terms of precision, completeness, and accuracy. Repeated analyses provided analytical precision. Duplicate samples provided sampling and analysis precision. Completeness was measured in terms of percent of scheduled samples that resulted in valid samples, beginning with the first valid site-specific sample collected and ending with the last scheduled site-specific sample. Accuracy of NMOC concentrations was reported as percent bias of audit samples referenced to an NIST SRM propane by EPA-QAD.

4.1 INTRODUCTION AND CONCLUSIONS

Completeness for the 1990 NMOC study was 94.9 percent. This value indicates that good communication and planning were maintained between the site personnel and the laboratory personnel. Precision for the 1990 NMOC study averaged 7.6% absolute percent difference of repeated analysis and compared to 14.2% for the 1989 study, 10.1% for the 1988 study, 9.61% for the 1987 study, 9.01% for the 1986 study, and 10% for the 1985 study. The absolute percent difference in 1990 was higher than in previous years and probably related to the fact that the overall average NMOC concentration for 1990 was lower than in previous years. For smaller values of NMOC concentrations, imprecision increases.

Bias of the Radian channels for the 1990 audit results ranged from -3.2% to +6.2 percent. In 1989 the accuracy determined from the external audit samples ranged from +1.3% to +4.5%, from 1.3% to 4.5% in 1988, and from -2.9% to -0.06% in 1987. In 1986 bias ranged from -0.52% to -3.3% and in 1985 bias ranged from -2.3% to +5.2 percent.

An initial multipoint performance evaluation was done with propane responses for each Radian channel. Daily calibration checks and in-house propane QC samples monitored instrument and operator performance. Duplicate site samples showed good overall sampling and analysis precision.

Data validation was performed on 100% of the 1990 NMOC data base, as described later in this section.

Calibration and drift determinations showed that the instrumentation was stable and that the calibration procedures were consistent. Canister cleanup results showed there was negligible carryover from one sample to the next. In-house QC samples of propane demonstrated that the analytical systems were in control.

Precision, accuracy, and completeness results for 1990 are comparable to results from previous years and indicate that the data quality are good and meet all of the data quality objectives of the QAPP.²

4.2 CALIBRATION AND INSTRUMENT PERFORMANCE

Initial performance assessments for NMOC were conducted with propane. Daily calibrations were checked with about 3.0 ppmC propane for the NMOC measurements.

4.2.1 Performance Assessment

An initial performance assessment was done on each Radian channel, using propane certified by EPA-QAD. EPA-QAD referenced the certified propane to an NIST propane CRM No. 1666B. The concentration of the propane used in the performance assessment ranged from 2.95 to 19.43 ppmC. The "zero" value was determined using cleaned, dried air from the canister cleanup system described in Section 3.0. Table 4-1 summarizes the performance assessments below. The FID responses for propane were linear, having coefficients of correlation from 0.999521 to 0.999992. Figures 4-1 through 4-4 show plots of the NMOC performance results for Radian Channels A, B, C, and D, respectively. The plots show the regression line.

4.2.2 Calibration Zero, Span, and Drift

Radian PDFID channels were tested daily for zero and span. Zero readings were measured using cleaned, dried air. The zero air was supplied by the same system that cleans air for the canister cleanup system. Span readings used a mixture of about 3.0 ppmC propane in dry air. Calibration factors were calculated from the span and zero readings for each Radian channel. Initial calibration factors were determined in the morning before any site samples were analyzed and final calibration factors were determined in the afternoon on randomly selected days after all the ambient air samples had been analyzed. Percent calibration factor drifts were determined based on

TABLE 4-1. 1990 PERFORMANCE ASSESSMENT SUMMARY, RADIAN CHANNELS

Radian Channel	Cases	Linear Regression Results ^a		
		Intercept	Slope	Coefficient of Correlation
A	5	-9.123	3424.023	0.999991
B	5	20.263	3311.255	0.999992
C	5	-157.444	3185.909	0.999521
D	5	260.600	3122.973	0.999927

^aFigures 4-1 through 4-4 plot propane area counts vs. concentration in ppmC.

Four Point Calibration – Channel A

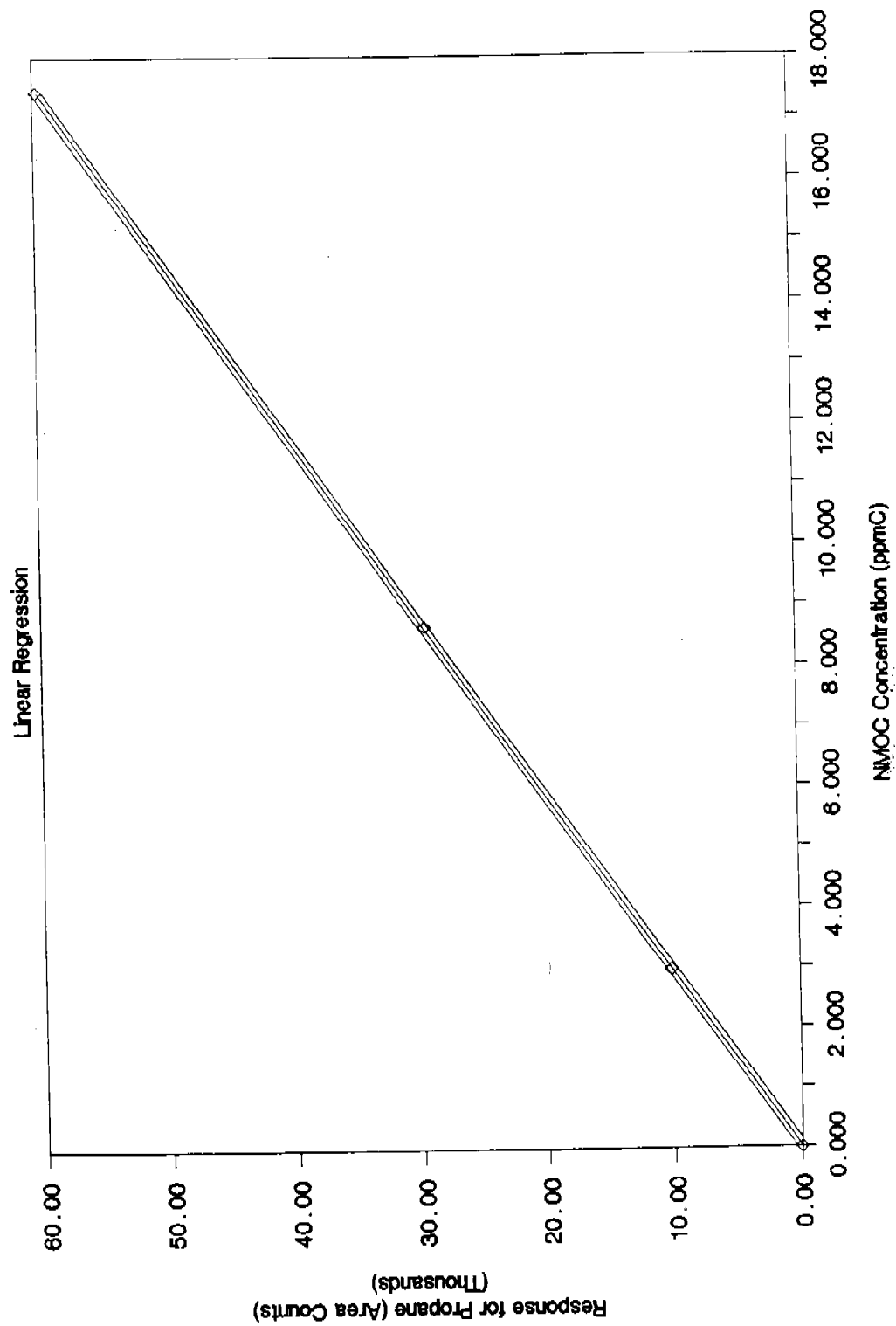


Figure 4-1. NMOC performance results, Channel A.

Four Point Calibration – Channel B

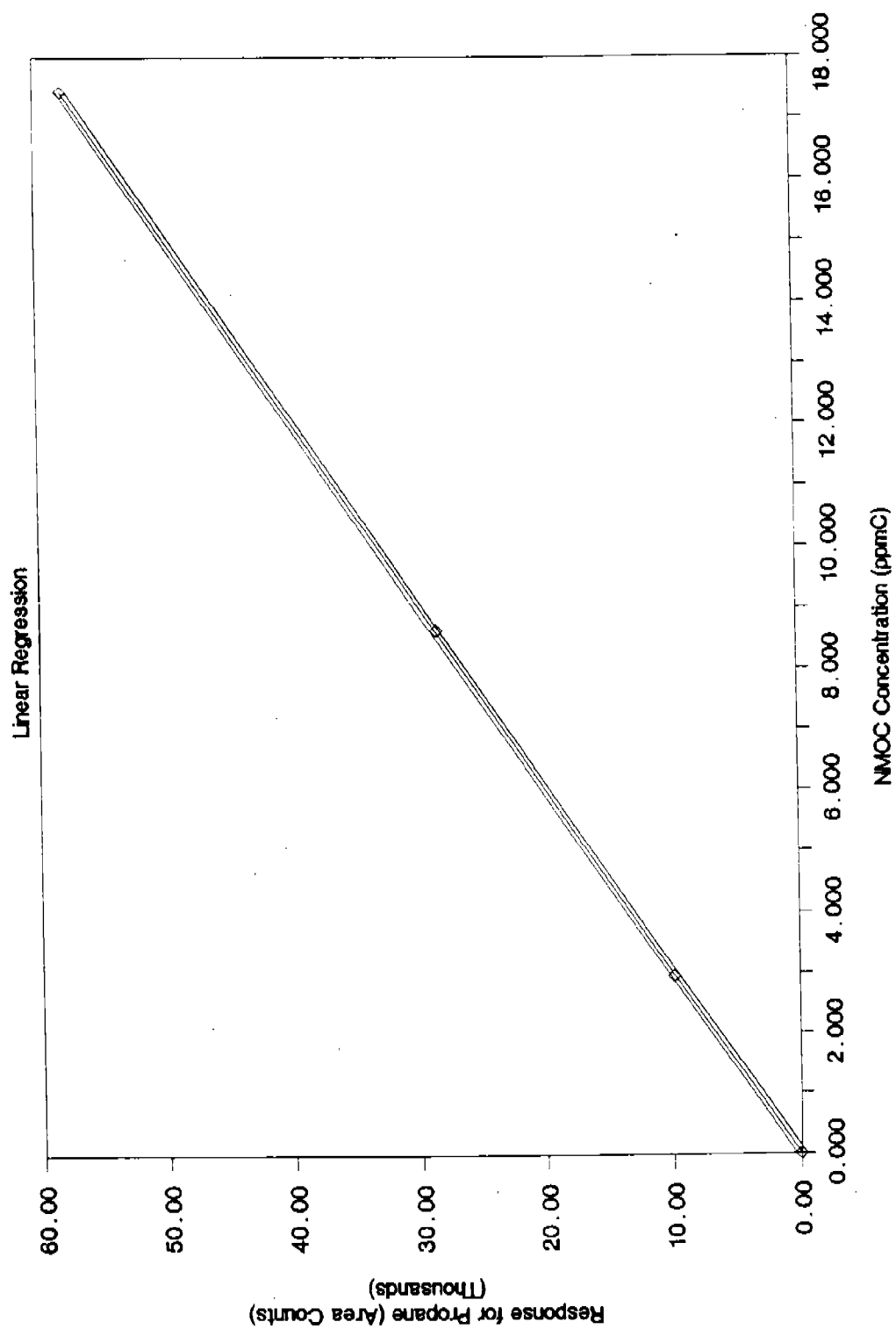


Figure 4-2. NMOC performance results, Channel B.

Four Point Calibration – Channel C

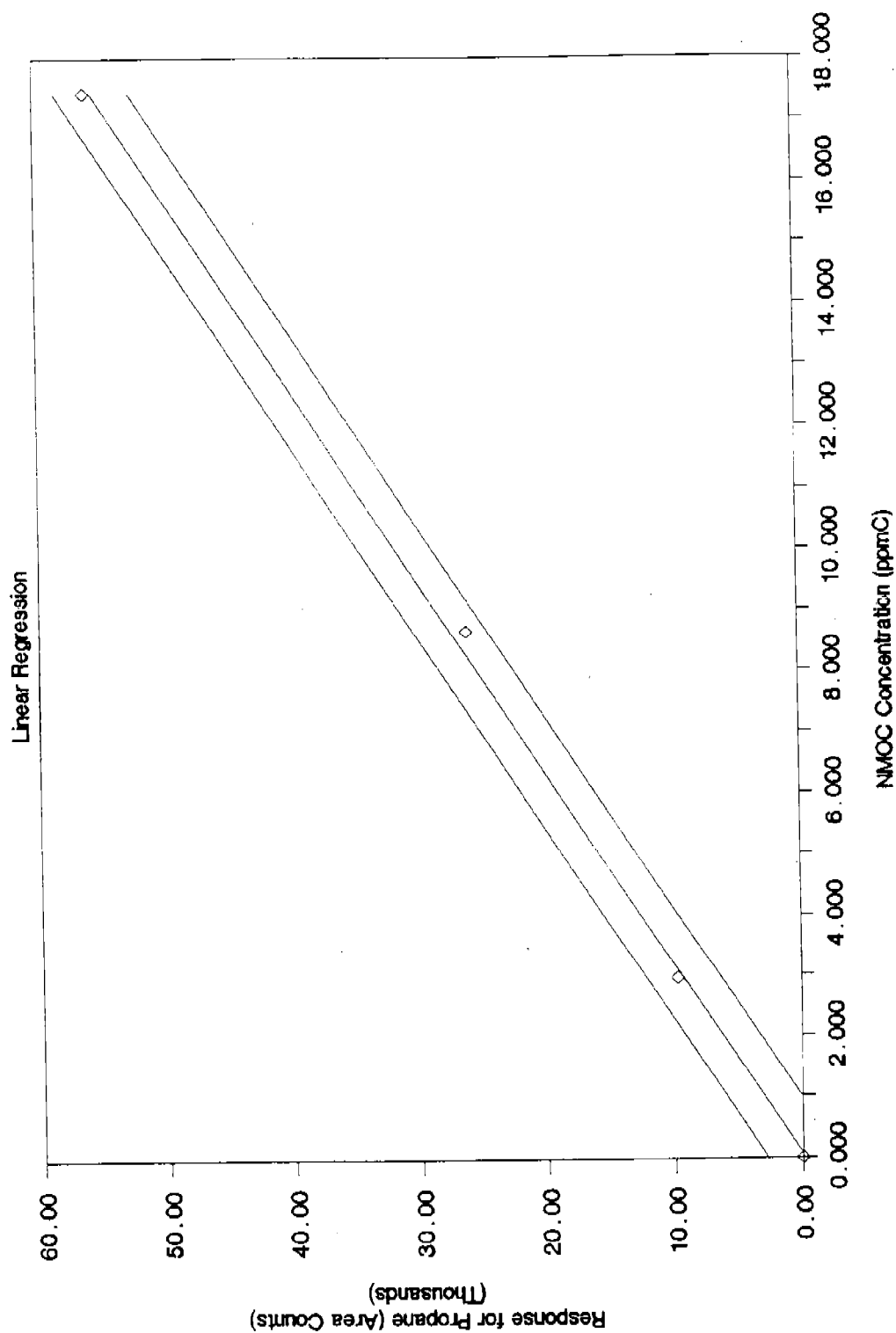


Figure 4-3. NMOC performance results, Channel C.

Four Point Calibration – Channel D

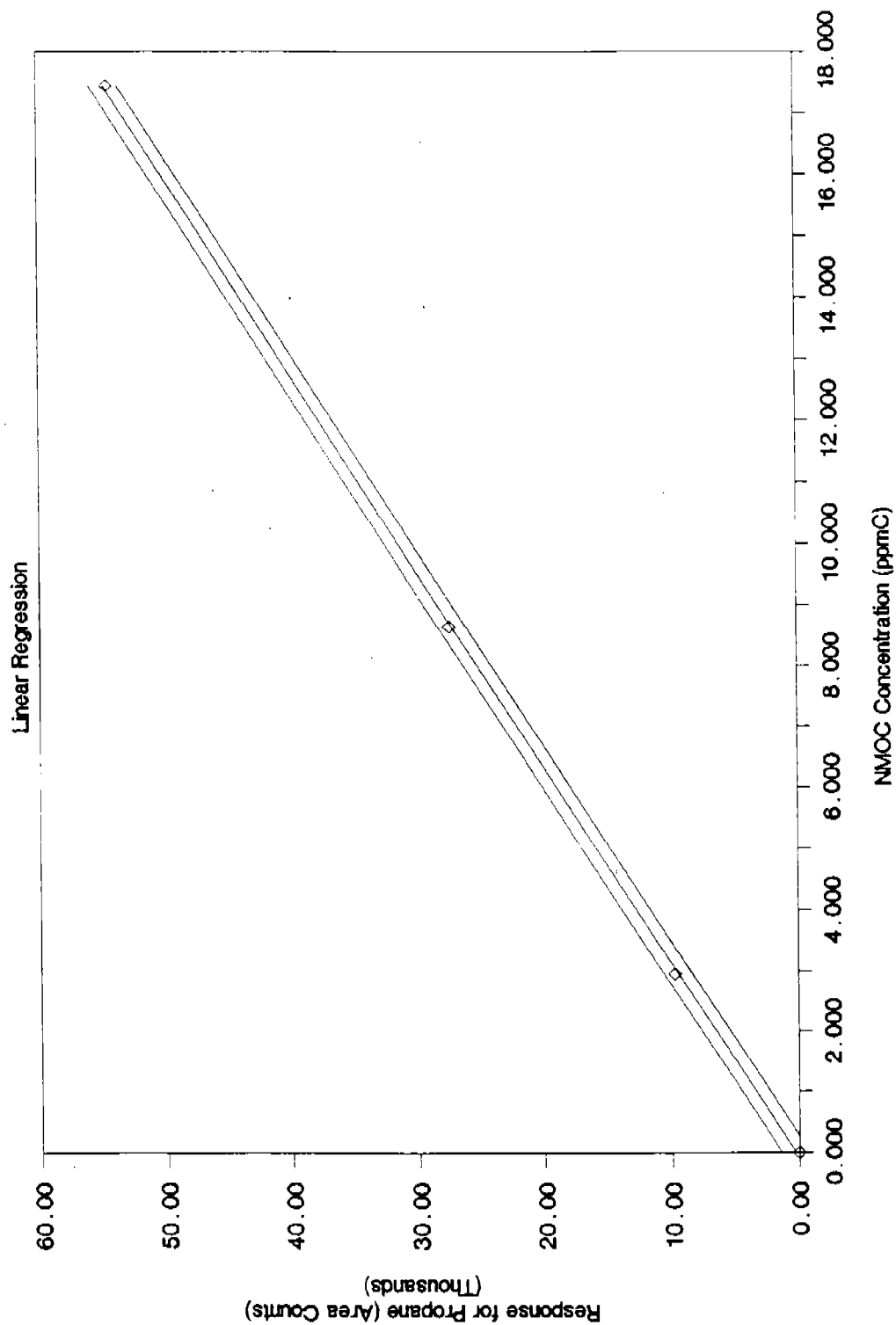


Figure 4-4 . NMOC performance results, Channel D .

the initial calibration factor. The data for zeros, calibration factors, and calibration factor drifts are given in Appendix F for each Radian channel and each calendar day of the analysis season. Figures 4-5 through 4-8 show plots for daily calibration zeros for Radian Channels A, B, C, and D. Figures 4-9 through 4-12 show the daily calibration span data as a function of the 1990 Julian date. Inspection of the percent drift figures shows that the maximum percent drift was 5.16. The average absolute % drift ranged from 0.643 for Channel B to 1.937 for Channel A.

4.2.3 Calibration Drift

Summary calibration factor drift data are given in Table 4-2. The table presents calibration factor drift, percent calibration factor drift, and absolute percent calibration factor drift. Calibration factors were calculated from an analysis of a propane-air mixture whose concentration was known and was referenced by the EPA-QAD to an NIST propane CRM No. 1666B reference standard as follows:

$$\text{calibration factor} = \frac{\text{concentration of propane standard (ppm)} \times 3 \text{ ppmC/ppm}}{(\text{propane standard response (area counts)} - \text{zero response (area counts)})}$$

Daily calibration factors ranged from 0.000288 ppmC/area count to 0.000313 ppmC/area count, depending on the channel. Maxima, minima, and mean values are given in Table 4-2 for calibration factor drift and percent calibration factor drift. If drift and percent drift are random variables and normally distributed, the mean values would be expected to be zero. The means shown in Table 4-2 for the drift and percent drift are approximately zero, showing little bias overall, or for any channel. The overall mean values shown in Table 4-2 were weighted according to the number of calibration drift data for each channel. The last two columns of Table 4-2 show the means and standard deviations of the absolute percent calibration factor drifts. The fact that the standard deviations are the same order of magnitude as the means indicates that the mean calibration factor drifts are not significantly different from zero.

DAILY CALIBRATION - ZERO

Radian Channel A

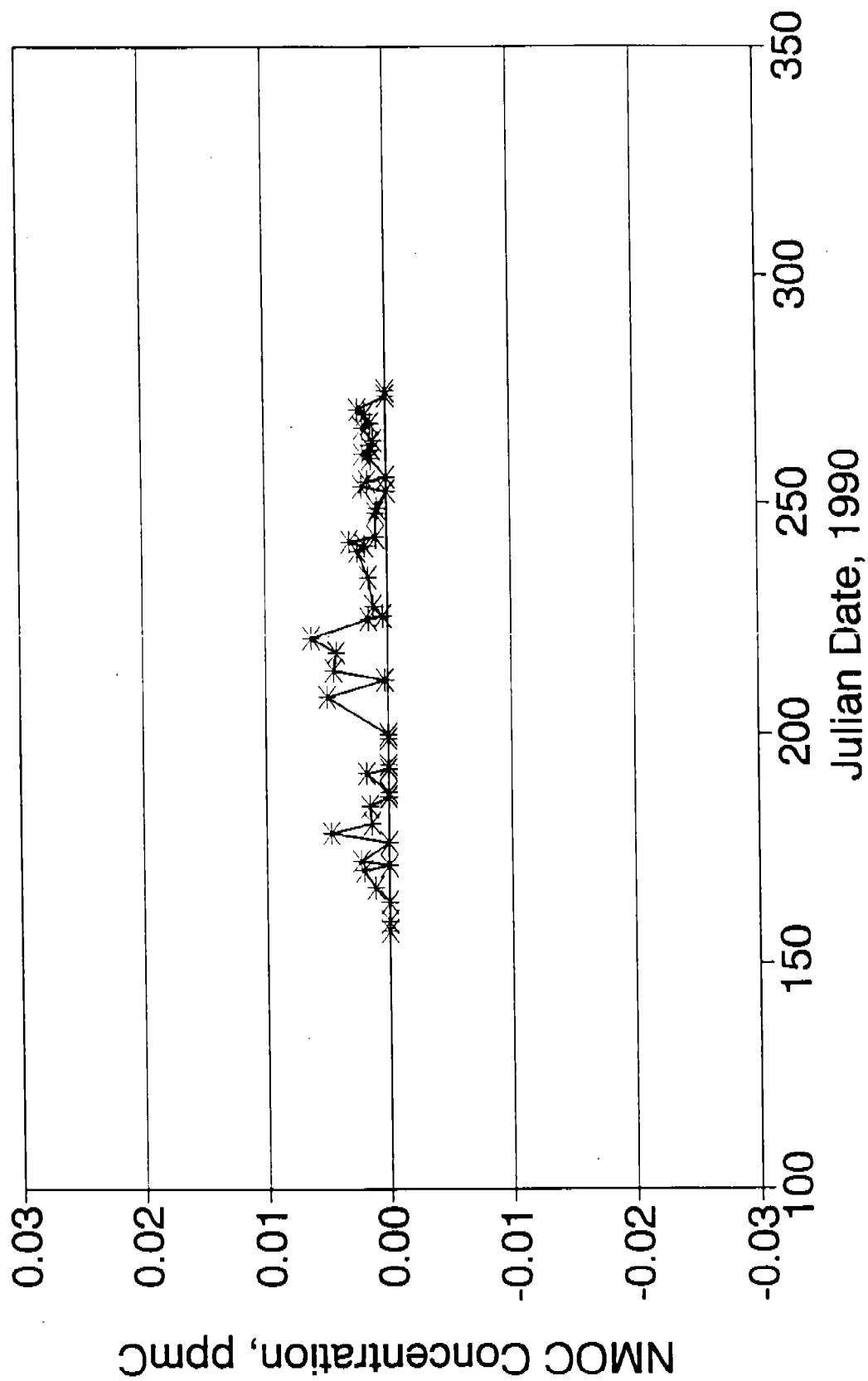


Figure 4-5. Daily calibration zero, Channel A.

DAILY CALIBRATION - ZERO

Radian Channel B

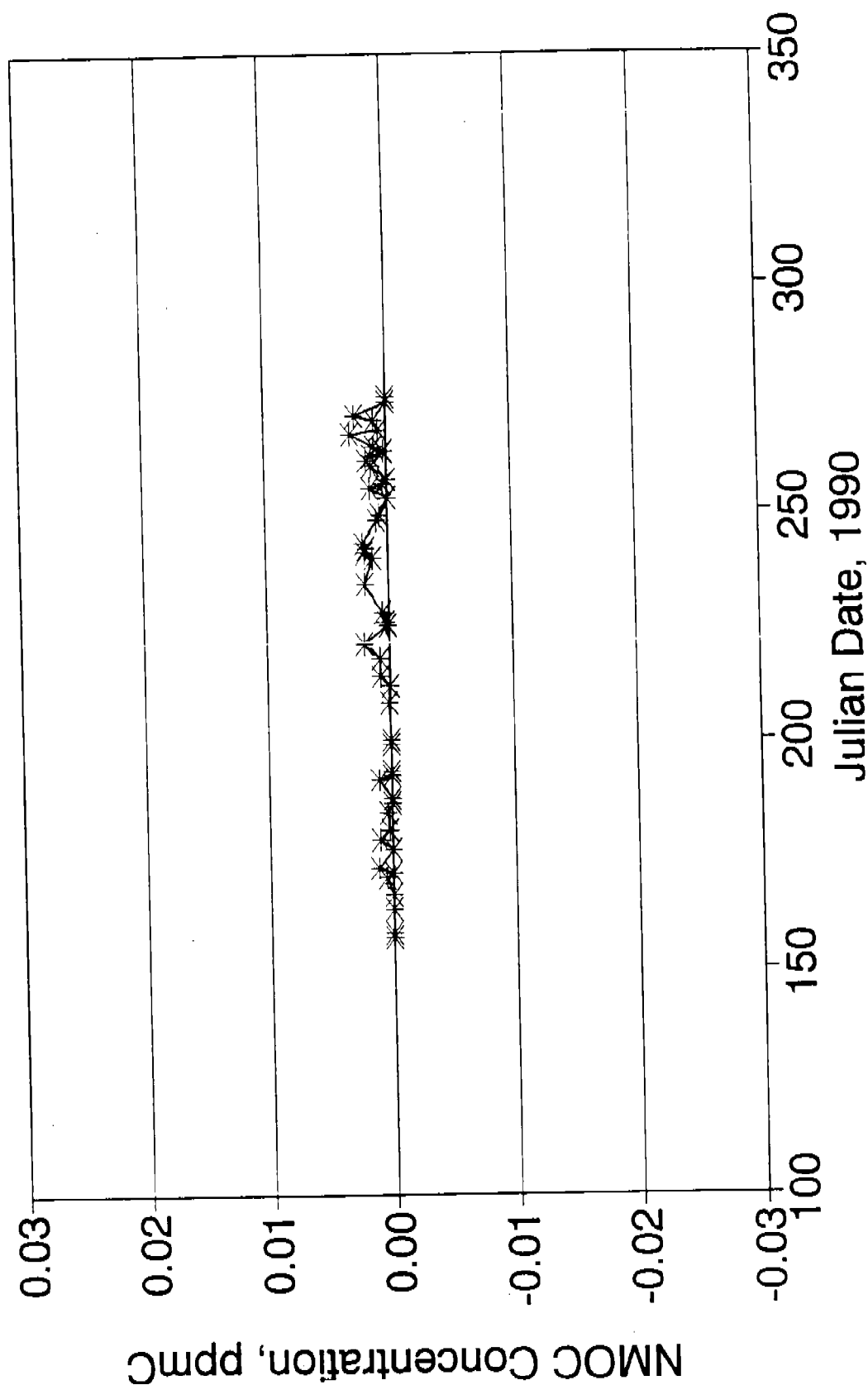


Figure 4-6 . Daily calibration zero, Channel B.

DAILY CALIBRATION - ZERO

Radian Channel C

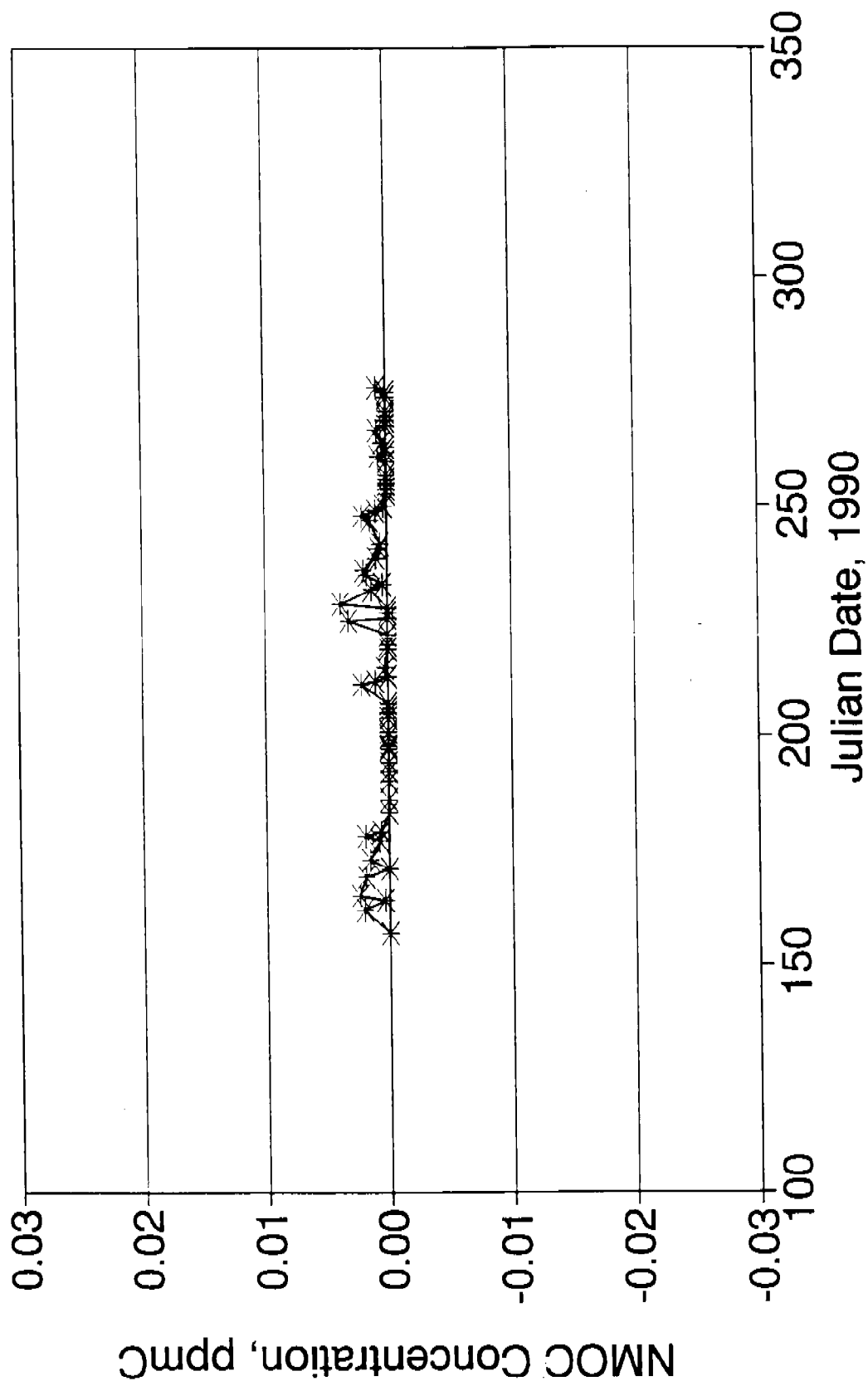


Figure 4-7. Daily calibration zero, Channel C.

DAILY CALIBRATION - ZERO

Radian Channel D

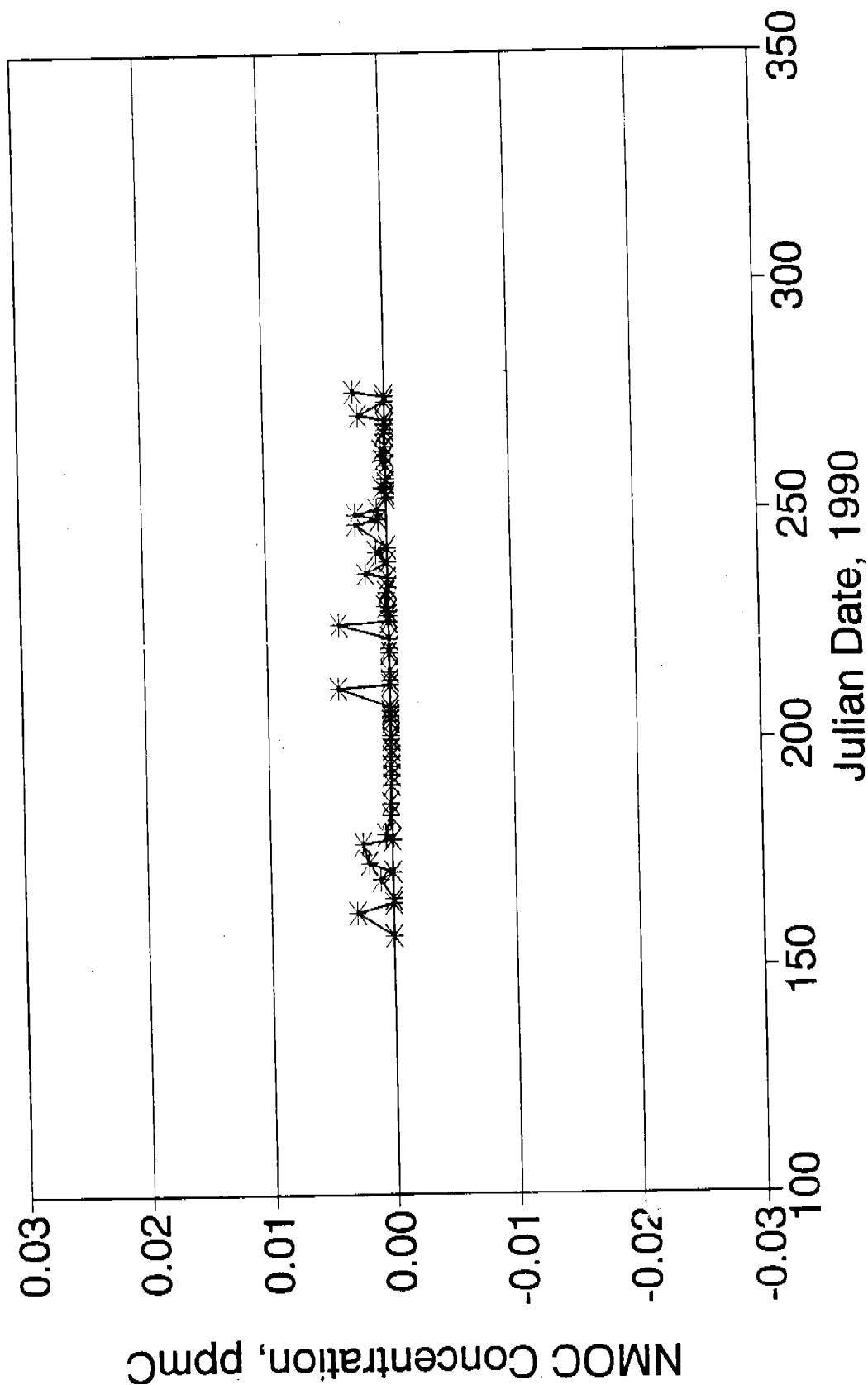


Figure 4-8. Daily calibration zero, Channel D.

DAILY CALIBRATION - SPAN

Radian Channel A

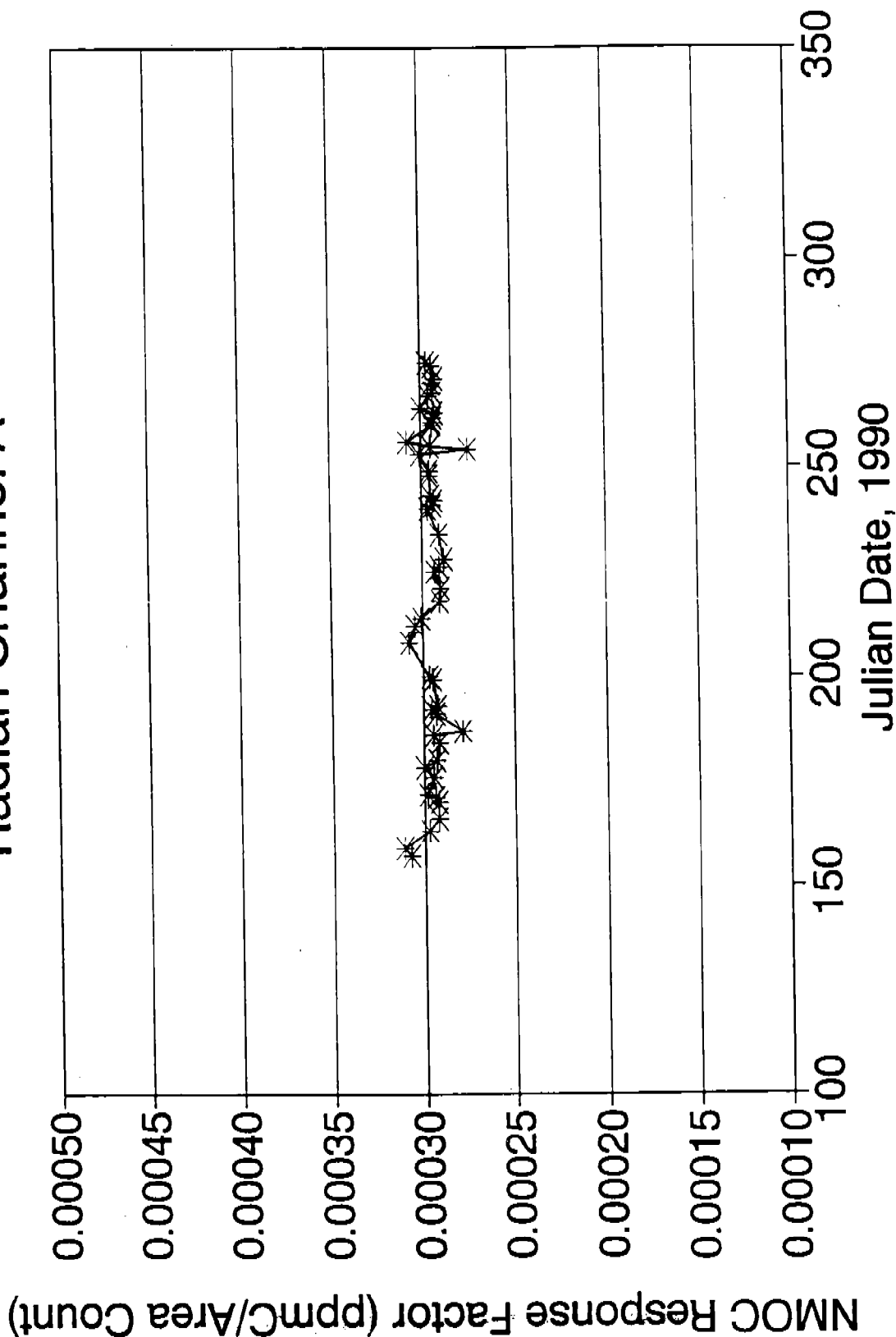


Figure 4-9. Daily calibration span, Channel A.

DAILY CALIBRATION - SPAN

Radian Channel B

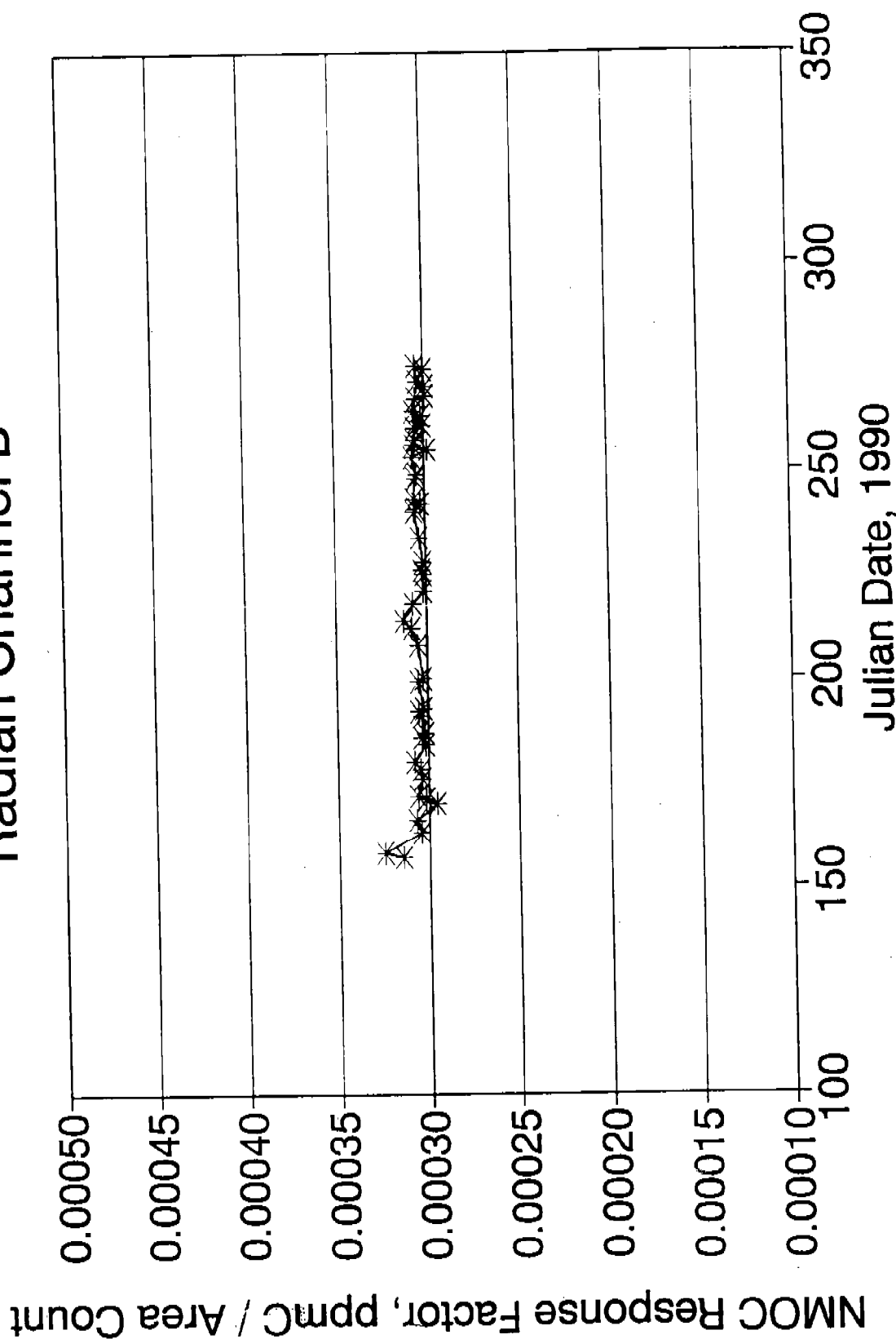


Figure 4-10. Daily calibration span, Channel B.

DAILY CALIBRATION - SPAN

Radian Channel C

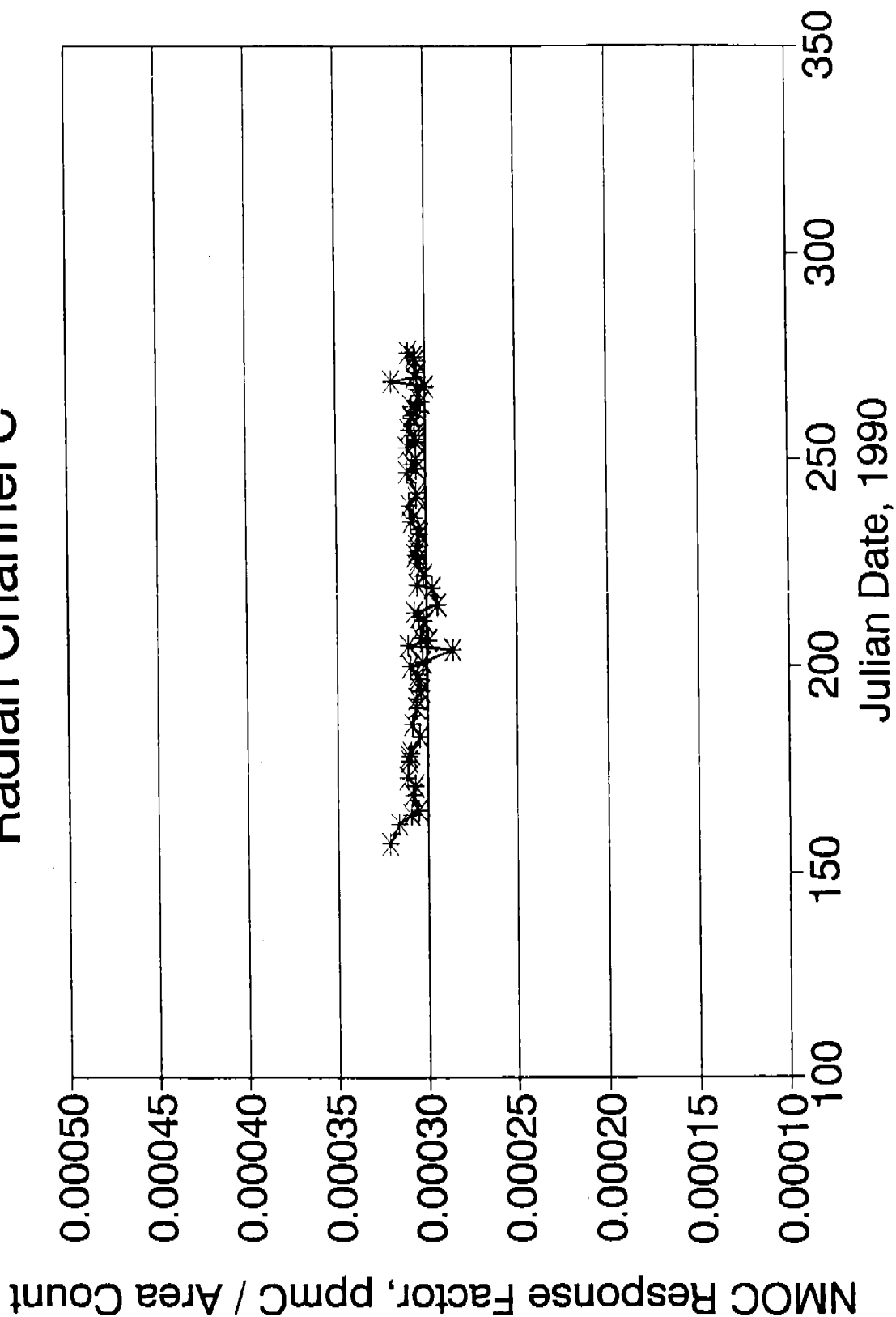


Figure 4-11. Daily calibration span, Channel C.

DAILY CALIBRATION - SPAN

Radian Channel D

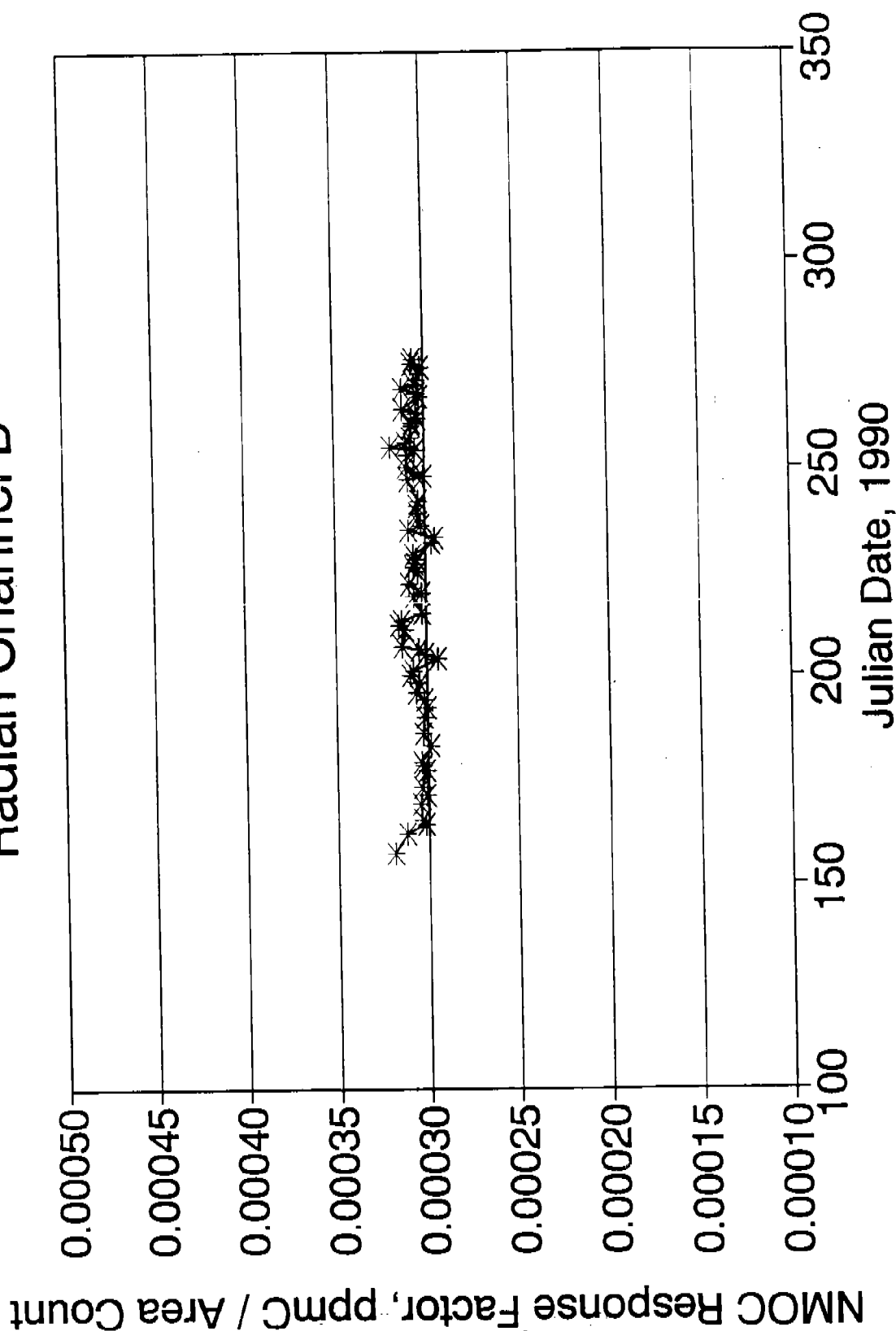


Figure 4-12. Daily calibration span, Channel D.

TABLE 4-2. SUMMARY NMOC CALIBRATION FACTOR DRIFT RESULTS

Radian Channel	Cases	Calibration Factor Drift ppmC/Area Count x 10 ⁶			Percent Factor Drift			Absolute Percent Factor Drift	
		Min	Mean	Max	Min	Mean	Max	Mean	Standard Deviation
A	48	-37.0	-1.0	16.0	-13.389	-0.581	5.161	1.937	3.696
B	48	-12.0	-2.0	1.0	-4.086	-0.577	0.427	0.643	1.104
C	64	-6.0	-1.0	7.0	-2.127	-0.197	2.288	0.652	0.786
D	64	-18.0	-1.0	8.0	-5.901	-0.344	2.396	0.710	1.333
Overall	224	-37.0	-1.3	16.0	-13.389	-0.425	5.161	0.986	1.330

Calibration factor drift was defined as final calibration factor for the day, minus initial calibration factor. Percent calibration factor drift was defined as the calibration factor drift divided by the initial calibration factor, expressed as a percentage. The absolute percent calibration factor drift is a measure of the calibration drift variability and averaged 0.9854% overall. The mean absolute percent calibration drift ranged from 0.643% for Radian Channel B to 1.937% for Radian Channel A.

4.3 IN-HOUSE QC SAMPLES

In-house quality control samples were prepared by Radian personnel. Local ambient sample results are presented and discussed in Section 4.4.4. In-house quality control samples were prepared by diluting dry propane with cleaned, dried air using calibrated flowmeters. The propane used for the in-house quality control samples was certified by the EPA-QAD against an NIST Reference Standard. The concentration of the in-house standard ranged from about 0.159 ppmC to 1.464 ppmC, but was set to average near the concentration levels that were being analyzed. The analyst did not know the concentration of the in-house standard prior to analysis.

The daily in-house QC data for each Radian channel are given in Appendix G, and include:

- Calendar date analyzed;
- Julian date for 1990;
- Radian ID Number;
- Calculated NMOC concentration in ppmC;
- Measured NMOC concentration in ppmC;
- Bias (measured NMOC-calculated NMOC); and
- % Bias ($\text{Bias} * 100 / \text{calculated NMOC}$).

Measured versus calculated NMOC concentrations in Figures 4-13 through 4-16 show excellent agreement. Table 4-3 summarizes the results of the linear regressions for the Radian in-house quality control data, showing regression intercepts near zero, and slopes and coefficients of correlation all near 1.0.

IN-HOUSE PROPANE QC RESULTS

Channel A

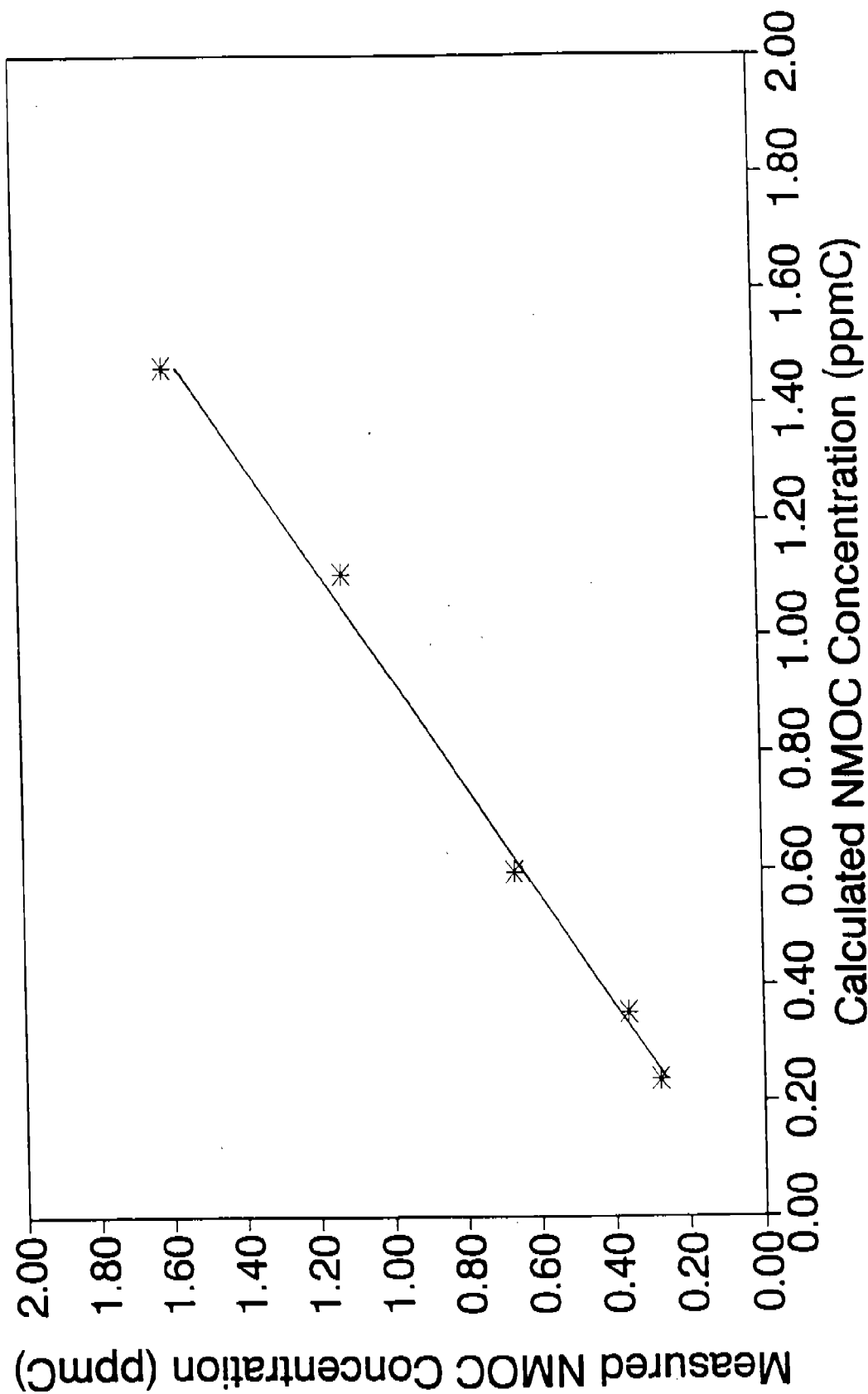


Figure 4-13. In-house quality control results, Channel A.

IN-HOUSE PROPANE QC RESULTS

Channel B

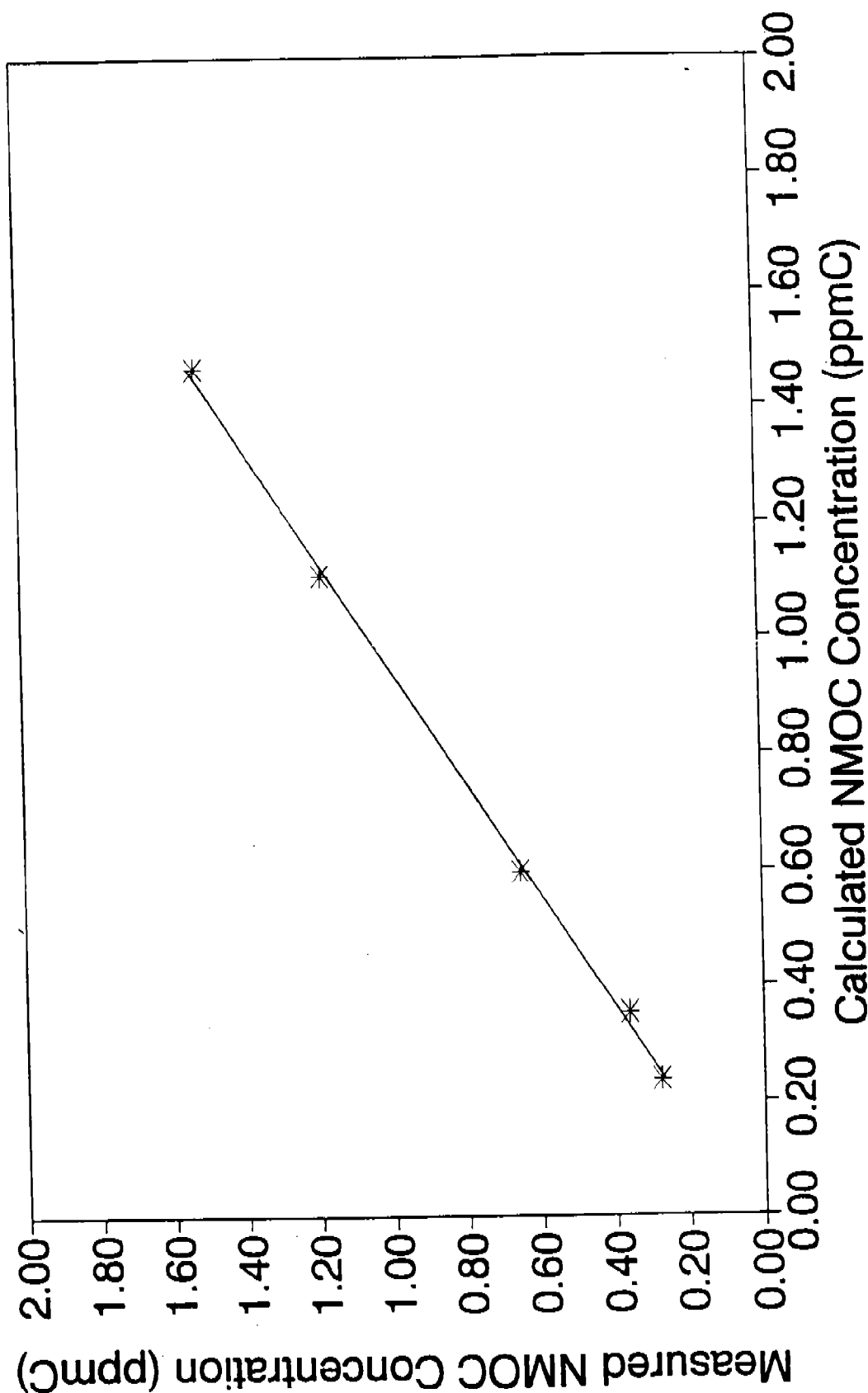


Figure 4-14. In-house quality control results, Channel B.

IN-HOUSE PROPANE QC RESULTS

Channel C

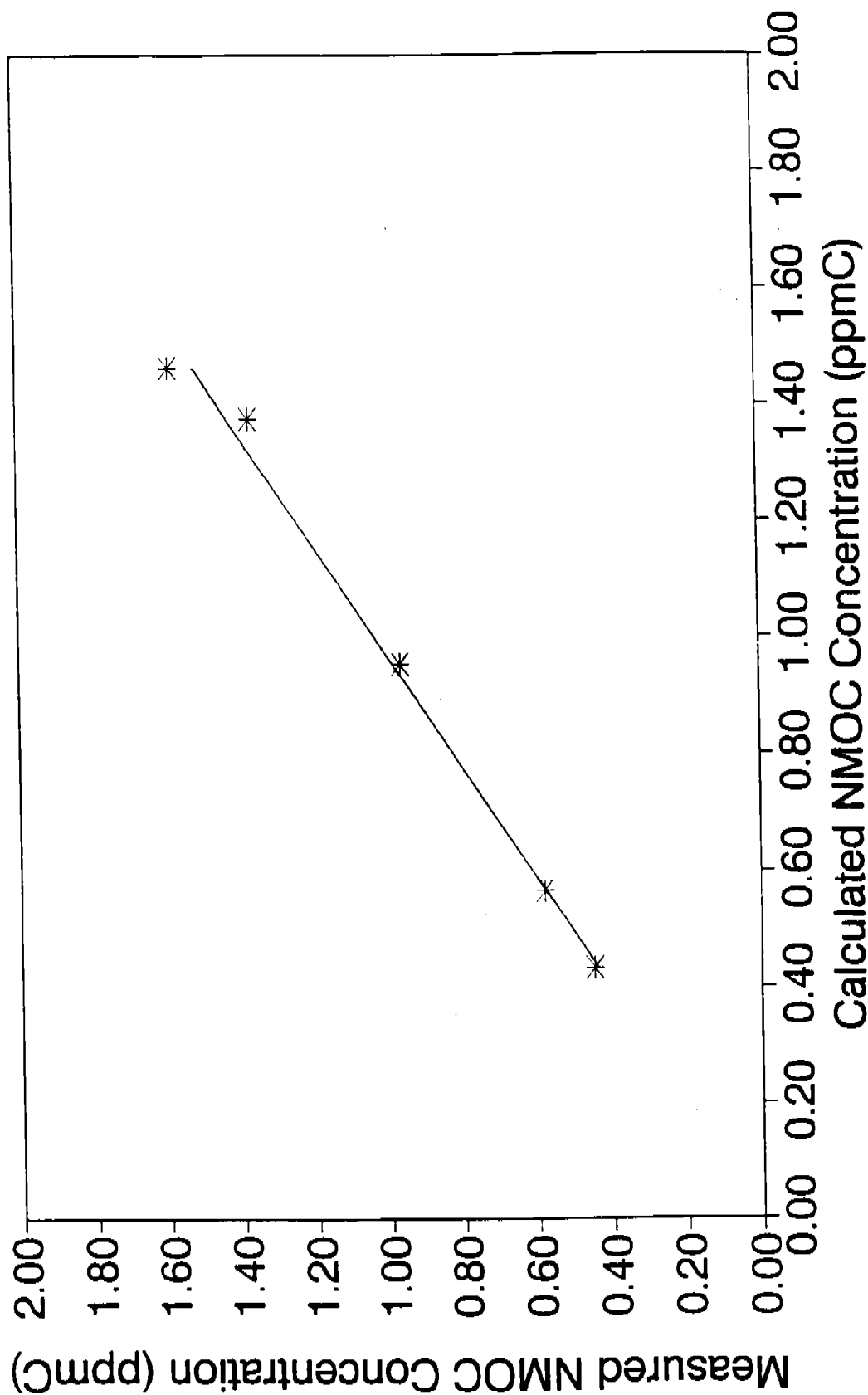


Figure 4-15. In-house quality control results, Channel C.

IN-HOUSE PROPANE QC RESULTS

Channel D

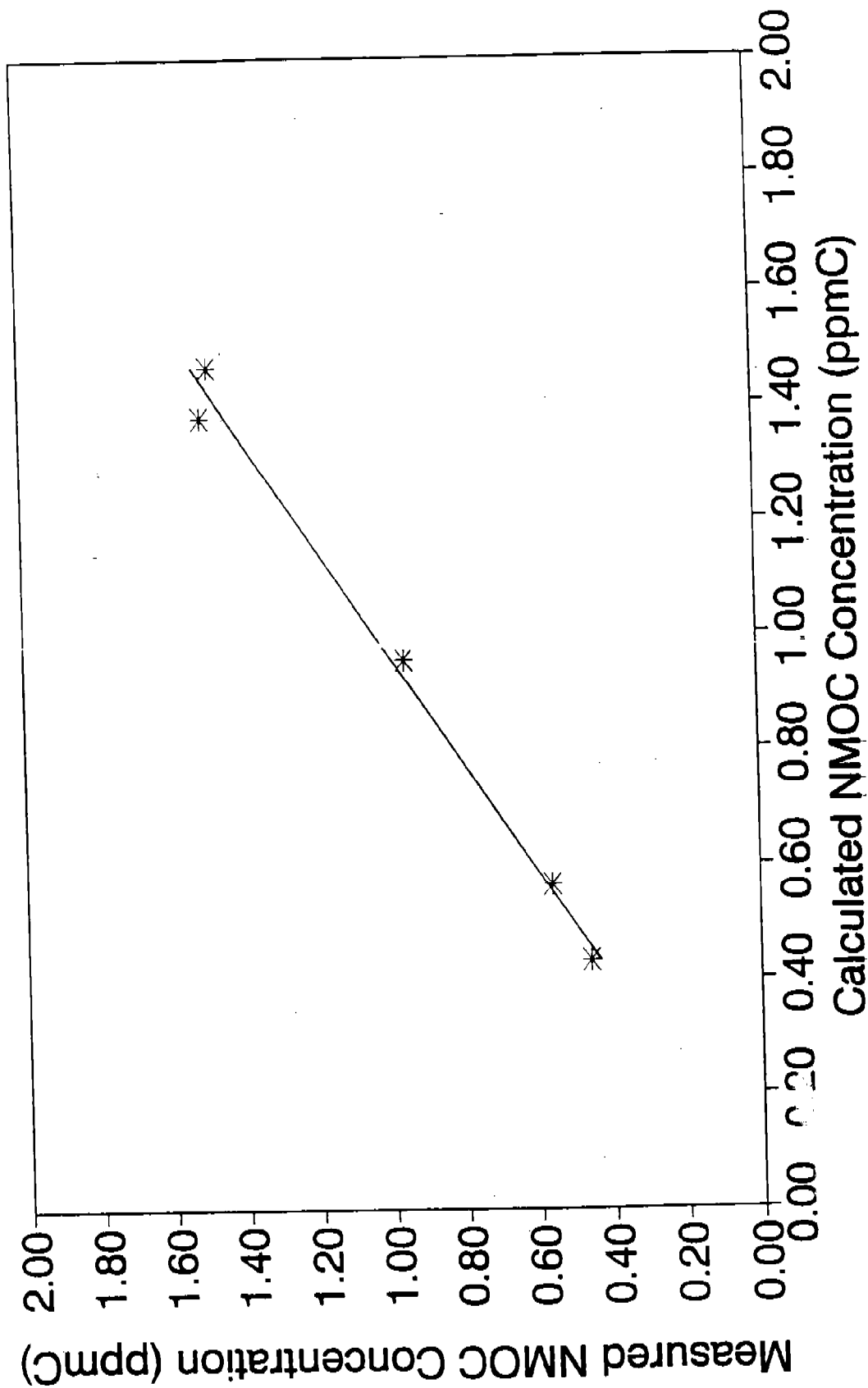


Figure 4-16. In-house quality control results, Channel D.

TABLE 4-3. LINEAR REGRESSION PARAMETERS FOR IN-HOUSE
QUALITY CONTROL DATA

Radian Channel	Cases	Intercept	Slope	Coefficient of Correlation
A	5	0.0086	1.060236	0.997253
B	5	0.0252	1.030042	0.999370
C	5	-0.0149	1.048497	0.995747
D	5	-0.0178	1.053398	0.995685

Tables 4-4 and 4-5 give statistics for in-house quality control measurements. DIFF is the ppmC difference between the measured and the calculated NMOC concentrations, and PCDIFF is the percentage of the difference relative to the calculated value. Both DIFF and PCDIFF may be considered to be bias terms, assuming that the calculated value is the correct NMOC concentration for the in-house QC sample. Overall, PCDIFF shows a mean bias of -1.43%, and ranges from -11.47% for Channel C to +8.45% for Channel A. ADIFF and APCDIFF, absolute values of DIFF and PCDIFF, respectively, were used as measures of precision. The absolute percent difference ranged from 8.08% for Channel B to 11.47% for Channel C and averaged 9.71 percent. These figures show excellent agreement and consistency for the in-house quality control data and include variability not only in the instrumental analysis but also in the apparatus and method used to generate the QC samples.

4.4 REPEATED ANALYSES

Two types of repeated analyses were conducted in this study. The first type of repeated analysis was conducted primarily to establish precision, and to determine if significant differences in precision existed among Radian (PDFID) channels and the EPA-QAD (PDFID) channel. Two samples were selected weekly from the received site samples for a second analysis on a Radian channel on the following workday. The second replicate analysis was performed on the day after the first analysis to allow time for the ambient air sample in the canister to equilibrate between analyses. At the beginning of the first analysis, the pressure in the canister is typically about 15 psig. At the beginning of the second analysis, the canister pressure is typically 9 psig.

The EPA-QAD channel randomly repeated analyses of the site samples already analyzed once by Radian. Shortly after the beginning of the 1988 NMOC Monitoring Program, the decision was made by Radian and the EPA to do repeated analyses only on duplicate samples, and to have the second analysis, not only on the day after the first analysis, but also on the same Radian channel as the first analysis. The purpose of the latter specification on replicate

TABLE 4-4. IN-HOUSE QUALITY CONTROL STATISTICS, BY RADIAN CHANNEL

Channel	Statistics	Variables			
		DIFF ^a	PCDIFF ^b	ADIFF ^c	APCDIFF ^d
A	Cases	5	5	5	5
	Minimum	0.012000	1.119134	0.012000	1.119134
	Maximum	0.136000	16.877637	0.136000	16.877637
	Mean	0.053880	8.452601	0.053880	8.452601
	Standard Dev.	0.051574	6.339540	0.051574	6.339540
	Std. Error	0.023065	2.835129	0.023065	2.835129
	Skewness	0.834878	0.115945	0.834878	0.115945
	Kurtosis	-0.720667	-1.320966	-0.720667	-1.320966
B	Cases	5	5	5	5
	Minimum	0.009000	2.549575	0.009000	2.549575
	Maximum	0.074900	17.721519	0.074900	17.721519
	Mean	0.047780	8.083983	0.047780	8.083983
	Standard Dev.	0.024624	6.033084	0.024624	6.033084
	Std. Error	0.011012	2.698077	0.011012	2.698077
	Skewness	-0.696930	0.826474	-0.696930	0.826474
	Kurtosis	-0.606814	-0.664283	-0.606814	-0.664283
C	Cases	5	5	5	5
	Minimum	-0.574000	-41.897810	0.011000	1.136364
	Maximum	-0.011000	-1.136364	0.574000	41.897810
	Mean	-0.147800	-11.473710	0.147800	11.473710
	Standard Dev.	0.242566	17.171850	0.242566	17.171850
	Std. Error	0.108479	7.679485	0.108479	7.679485
	Skewness	-1.377939	-1.430692	1.377939	1.430692
	Kurtosis	0.062944	0.153121	0.062944	0.153121
D	Cases	5	5	5	5
	Minimum	-0.705000	-46.968688	0.001000	0.104384
	Maximum	0.001000	0.177620	0.705000	46.968688
	Mean	-0.149600	-10.771777	0.150000	10.842825
	Standard Dev.	0.310689	20.382069	0.310448	20.334924
	Std. Error	0.138944	9.115138	1.495343	9.094055
	Skewness	-1.494924	-1.448239	1.495343	1.450727
	Kurtosis	0.243176	0.174921	0.243736	0.178461

^aDIFF = Measured NMOC concentration - Calculated NMOC concentration, ppmC.^bPCDIFF = Absolute value of DIFF.^cADIFF = DIFF/calculated NMOC concentration x 100.^dAPCDIFF = Absolute value of PCDIFF.

TABLE 4-5. OVERALL IN-HOUSE QUALITY CONTROL STATISTICS

Statistics	DIFF ^a	PCDIFF ^b	ADIFF ^c	APCDIFF ^d
Cases	20	20	20	20
Minimum	-0.705000	-46.968688	0.001000	0.104384
Maximum	0.136000	17.721519	0.705000	46.968688
Mean	-0.048935	-1.427226	0.099865	9.713280
Standard Dev.	0.209472	16.269424	0.189476	12.943140
Standard Error	0.046839	3.637954	0.042368	2.894174
Skewness	-2.425102	-1.784011	2.546347	2.013069
Kurtosis	4.577324	2.768662	4.963889	3.018044

^aDIFF = Measured NMOC concentration - Calculated NMOC concentration, ppmC.

^bPCDIFF = Absolute value of DIFF.

^cADIFF = DIFF/calculated NMOC concentration x 100.

^dAPCDIFF = Absolute value of PCDIFF.

analyses was to avoid any bias that may be caused by a different analysis channel. None of the site samples selected for repeated analyses by Radian channels was analyzed a third time by the EPA-QAD channel.

All replicate analyses were performed on duplicate samples, but not all the analyses on duplicate samples were replicated. Each analysis consisted of two or three consecutive injections from a canister that was connected to the GC. After the first analysis, the canister valve was closed, the canister was disconnected from the GC, and the canister was stored at laboratory temperature overnight. The second replicate analysis on the sample in the canister was performed on the next day, or the following Monday if the first analysis was on Friday. Replicate analyses were performed on the same analytical channel, i.e., Radian Channel A, B, C, or D, for a given duplicate sample. By conducting repeated analyses of the duplicate samples it was possible to investigate the relative magnitude of the duplicate sampling precision and the analytical precision. The results for this investigation are given in Section 4.5.

The second type of comparative analysis was done on local ambient samples collected by EPA-QAD personnel in Raleigh, in Research Triangle Park, or near Research Triangle Park, North Carolina. These samples were taken once weekly in duplicate at an initial pressure of about 35 psig. Each local ambient sample, called a round-robin sample, was analyzed by all four Radian channels and the EPA-QAD channel. The purposes of these studies were:

- to compare the precision of all the channels; and
- to compare the results among Radian channels.

4.4.1 Site Sample Results

Figure 4-17 compares the EPA-QAD analyses with Radian analyses of the same site samples. Orthogonal regression parameters for the three data sets are summarized in Table 4-6.

Summary statistics of the comparative analyses for Radian channels versus the EPA-QAD channel are given in Table 4-7. The table gives DIFF, the difference between the Radian NMOC concentration and the QAD NMOC

1990 NMOC Program

Orthogonal Regression

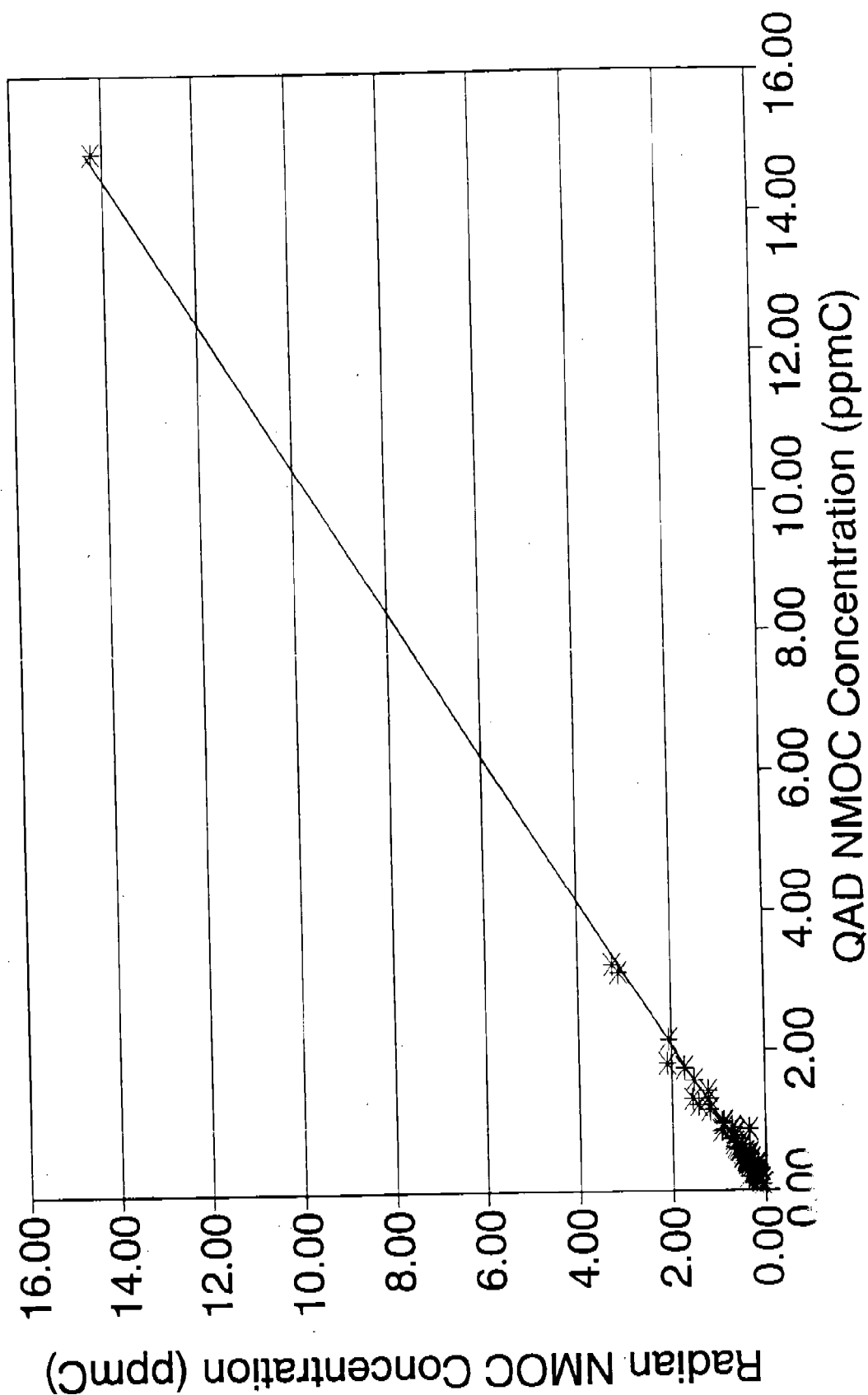


Figure 4-17. Orthogonal regression comparing QAD with Radian NMOC analyses

TABLE 4-6. ORTHOGONAL REGRESSION PARAMETERS FOR
REPEATED ANALYSES OF SITE SAMPLES

Channel Pair (X-Y)	Cases	Intercept	Slope	Coefficient of Correlation
QAD-Radian	203	-0.01883	0.969127	0.99763
Radian-QAD	203	0.01943	1.031856	0.99763

TABLE 4-7. SUMMARY STATISTICS OF COMPARITIVE ANALYSES
FOR RADIAN vs. QAD CHANNELS

Statistics	Variables			
	DIFF	ADIFF	PDIFF	APDIFF
Cases	203	203	203	203
Minimum	-0.658000	0.000000	-92.411467	0.000000
Maximum	0.245000	0.658000	47.584973	92.411467
Mean	-0.041298	0.058322	-11.649193	13.645930
Standard Dev.	0.084773	0.074042	16.276369	14.634290
Std. Error	0.005950	0.005197	1.142377	1.027126
Skewness	-2.785000	4.567531	-1.447560	2.219136
Kurtosis	19.670167	29.306331	5.137470	6.636771

DIFF = Radian NMOC concentration - QAD NMOC cocentration, ppmC.
ADIFF = Absolute value of DIFF.
PDIFF = DIFF/((Radian NMOC conc. + QAD NMOC conc.)/2) x 100.
APDIFF = Absolute value of PDIFF.

concentration in ppmC; and PDIFF, the percent difference relative to the mean of the Radian and QAD analyses. ADIFF and APDIFF are the absolute values of DIFF and PDIFF, respectively. The mean percent difference shows Radian NMOC concentrations to average 11.65% lower than the QAD NMOC concentration. This is an average bias figure for the Radian analyses relative to a mean NMOC concentration. The average absolute percent difference is 13.64, which is a measure of the precision.

In 1985, the mean percent difference showed Radian NMOC concentrations to average 0.49% higher than QAD, and 3.77 lower in 1986. In 1987, the mean percent differences showed Radian concentrations to average 4.48% lower than the QAD NMOC concentration. In 1988, the percent difference was shown to be 1.674 percent. In 1989, the percent difference was shown to be 11.11 percent. The average absolute percent difference was 10.5% in 1985, 14.8% in 1986, 14.07% in 1987, 11.76% in 1988, and 13.92% in 1989. The agreement among the precision results is good, and shows that the instruments and operating procedures were consistent for those years.

Summary statistics are given for the same data in Table 4-8 by Radian channel. The data show a mean absolute percent difference ranging from 8.05% for Channel A to 17.00% for Channel B. The mean percent differences range from -15.70% for Channel C to -4.49% for Channel A.

Of NMOC concentration measurements, the comparison between Radian and the EPA-QAD channel represents between-laboratory comparisons for the PDFID method.

4.4.2 Local Ambient Samples

Table 4-9 presents the overall statistics for local ambient samples. These data include comparisons among Radian channels and EPA channels. The mean differences and the mean percent differences are both relatively small, which indicates that they are random variables. The overall mean absolute percent difference (APDIFF) is 10.79, which is slightly higher than the precision for repeated analyses (7.59 percent).

Table 4-10 presents the same information comparing each Radian channel to the QAD results and to other Radian channels. Note from the definition of percent difference, PCDIFF, in this table that the Radian-QAD comparisons are

TABLE 4-8. SUMMARY STATISTICS OF COMPARITIVE ANALYSES
FOR RADIAN vs. QAD CHANNELS, BY RADIAN CHANNELS

Variables					
Channel	Statistics	DIFF	ADIFF	PCDIFF	APCDIFF
A	Cases	40	40	40	40
	Minimum	-0.094000	0.000000	-38.532110	0.000000
	Maximum	0.245000	0.245000	12.522361	38.532110
	Mean	0.000493	0.038608	-4.492402	8.054578
	Standard Dev.	0.057657	0.042377	10.406435	7.902742
	Std. Error	0.009116	0.006700	1.645402	1.249533
	Skewness	1.883789	3.026966	-1.025228	1.816715
	Kurtosis	6.310887	12.127198	1.312598	3.887183
B	Cases	39	39	39	39
	Minimum	-0.548000	0.004000	-92.411467	0.472255
	Maximum	0.038000	0.548000	4.679245	92.411467
	Mean	-0.045762	0.052890	-10.603389	11.458382
	Standard Dev.	0.095242	0.091374	17.656426	17.099425
	Std. Error	0.015251	0.014632	2.827291	2.738099
	Skewness	-3.999361	4.362992	-3.033304	3.250218
	Kurtosis	18.166997	20.505008	10.415898	11.519870
C	Cases	59	59	59	59
	Minimum	-0.658000	0.002000	-84.782609	0.395517
	Maximum	0.227000	0.658000	15.802297	84.782609
	Mean	-0.061363	0.074990	-15.697656	16.996967
	Standard Dev.	0.104481	0.095006	17.529110	16.249825
	Std. Error	0.013601	0.012369	2.282096	2.115547
	Skewness	-2.920211	4.134173	-1.259254	1.608231
	Kurtosis	16.994923	22.256604	2.611505	3.585038
D	Cases	65	65	65	65
	Minimum	-0.287000	0.001000	-66.277940	0.085800
	Maximum	0.160000	0.287000	47.584973	66.277940
	Mean	-0.046123	0.058585	-13.006094	15.357580
	Standard Dev.	0.062285	0.050540	16.029352	13.755043
	Std. Error	0.007726	0.006269	1.988196	1.706103
	Skewness	-0.457410	2.321424	-0.198840	1.591507
	Kurtosis	5.272974	6.759744	3.791189	2.585024

DIFF = Radian NMOC concentration - QAD concentration, ppmC.

ADIFF = Absolute value of DIFF.

PCDIFF = $\text{DIFF} / ((\text{Radian NMOC conc.} + \text{QAD NMOC conc.}) / 2) \times 100$.

APCDIFF = Absolute value of PCDIFF.

TABLE 4-9. OVERALL STATISTICS FOR LOCAL AMBIENT SAMPLES

Statistics	Variables			
	DIFF	ADIFF	PDIFF	APDIFF
Cases	285	285	285	285
Minimum	-0.128500	0.000000	-53.953500	0.000000
Maximum	0.146000	0.146000	63.478260	63.478260
Mean	0.004720	0.023733	3.098817	10.792590
Standard Dev.	0.036019	0.027468	15.598875	11.664957
Std. Error	0.002134	0.001627	0.923998	0.690972
Skewness	-0.233562	2.163849	0.003183	1.834720
Kurtosis	3.958082	4.970242	2.680728	3.244192

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.

ADIFF = Absolute value of DIFF.

PDIFF = $\text{DIFF} / ((\text{NMOC concentration on Channel Y} + \text{NMOC concentration on Channel X}) / 2) \times 100$.

APDIFF = Absolute value of PDIFF.

TABLE 4-10. STATISTICS FOR LOCAL AMBIENT SAMPLES, BY CHANNEL PAIR

Channel Pair (X-Y)	Statistics	Variables			
		DIFF	ADIFF	PCDIFF	APCDIFF
A-QAD	Cases	28	28	28	28
	Minimum	-0.009000	0.000000	-33.962300	0.000000
	Maximum	0.101000	0.101000	43.983400	43.983400
	Mean	0.020946	0.022804	8.568138	11.482086
	Standard Dev.	0.026247	0.024589	15.214099	13.072088
	Std. Error	0.004960	0.004647	2.875194	2.470392
	Skewness	1.336522	1.572985	0.169040	1.202195
	Kurtosis	1.557195	2.177765	1.554233	0.145295
B-A	Cases	30	30	30	30
	Minimum	-0.068500	0.001000	-18.357500	0.214592
	Maximum	0.135000	0.135000	46.481880	46.481880
	Mean	0.009117	0.021483	5.607768	8.805819
	Standard Dev.	0.037609	0.031984	13.489326	11.587796
	Std. Error	0.006866	0.005839	2.462803	2.115632
	Skewness	1.544978	2.341493	1.580053	2.166382
	Kurtosis	4.174428	4.916535	2.810512	3.967172
B-QAD	Cases	28	28	28	28
	Minimum	-0.054000	0.001000	-24.000000	0.547945
	Maximum	0.146000	0.146000	63.478260	63.478260
	Mean	0.029536	0.034679	14.177094	16.620156
	Standard Dev.	0.044426	0.040388	19.134648	16.973759
	Std. Error	0.008396	0.007633	3.616109	3.207739
	Skewness	1.285584	1.718092	0.843743	1.303612
	Kurtosis	1.434881	1.742346	0.582839	0.784650
C-A	Cases	29	29	29	29
	Minimum	-0.128500	0.002000	-29.894700	0.209644
	Maximum	0.041000	0.128500	30.943400	30.943400
	Mean	-0.010397	0.021431	-1.766509	8.771303
	Standard Dev.	0.035428	0.029857	11.991603	8.206534
	Std. Error	0.006579	0.005544	2.226785	1.523915
	Skewness	-1.864971	2.388067	0.344951	1.218734
	Kurtosis	3.620013	5.154058	0.982810	1.030121

(Continued)

TABLE 4-10. CONTINUED

Channel Pair (X-Y)	Statistics	Variables			
		DIFF	ADIFF	PCDIFF	APCDIFF
C-B	Cases	29	29	29	29
	Minimum	-0.118000	0.001000	-53.953500	0.470588
	Maximum	0.039000	0.118000	29.657790	53.953490
	Mean	-0.020103	0.027828	-7.585464	12.445828
	Standard Dev.	0.040070	0.034959	18.012517	14.953731
	Std. Error	0.007441	0.006492	-0.943821	1.574649
	Skewness	-1.309112	1.649387	-0.943821	1.574649
	Kurtosis	0.947050	1.531250	1.112597	1.300876
C-D	Cases	29	29	29	29
	Minimum	-0.069000	0.000000	-25.000000	0.000000
	Maximum	0.025000	0.069000	20.080320	25.000000
	Mean	-0.015486	0.019762	-4.467421	7.792632
	Standard Dev.	0.022088	0.018214	8.652038	5.712668
	Std. Error	0.004102	0.003382	1.606643	1.060816
	Skewness	-0.565194	1.090211	0.663244	1.199562
	Kurtosis	-0.019772	0.482245	1.705929	1.605557
C-QAD	Cases	27	27	27	27
	Minimum	-0.104000	0.002000	-48.275900	0.479616
	Maximum	0.062000	0.104000	43.356640	48.275860
	Mean	0.010370	0.024222	6.708410	12.749633
	Standard Dev.	0.031466	0.022192	16.645594	12.450063
	Std. Error	0.006056	0.004271	3.203446	2.396016
	Skewness	-1.948687	1.877617	-0.883131	1.464378
	Kurtosis	5.027928	4.344986	3.154209	1.520432
D-A	Cases	29	29	29	29
	Minimum	-0.059500	0.000000	-20.095700	0.000000
	Maximum	0.037000	0.059500	19.548870	20.095690
	Mean	0.005090	0.016841	2.703663	7.131970
	Standard Dev.	0.021945	0.014651	8.589304	5.354010
	Std. Error	0.004075	0.002721	1.594994	0.994215
	Skewness	-1.126078	1.014888	-0.745355	0.877557
	Kurtosis	1.388990	0.605716	0.704756	0.198807

(Continued)

TABLE 4-10. CONTINUED

Channel Pair (X-Y)	Statistics	Variables			
		DIFF	ADIFF	PCDIFF	APCDIFF
D-B	Cases	29	29	29	29
	Minimum	-0.110000	0.000000	-40.609100	0.000000
	Maximum	0.032000	0.110000	9.722222	40.609140
	Mean	-0.004617	0.019452	-3.163752	8.525078
	Standard Dev.	0.034177	0.028254	14.370359	11.899649
	Std. Error	0.006346	0.005247	2.668509	2.209709
	Skewness	-1.970547	2.075796	-1.793970	1.938092
	Kurtosis	2.926870	3.249982	1.863676	2.285483
D-QAD	Cases	27	27	27	27
	Minimum	-0.043900	0.002000	-24.000000	2.113606
	Maximum	0.066000	0.066000	30.534350	30.534350
	Mean	0.025856	0.029700	11.520043	14.269380
	Standard Dev.	0.022241	0.016519	12.254973	8.749483
	Std. Error	0.004280	0.003179	2.358471	1.683839
	Skewness	-0.917508	0.321019	-0.717170	0.450707
	Kurtosis	2.049126	-0.313723	0.932706	-1.206561

DIFF = NMOC concentration on Channel Y - NMOC concentration on Channel X, ppmC.

ADIFF = Absolute value of DIFF.

PCDIFF = $\text{DIFF} / ((\text{NMOC concentration on Channel X} + \text{NMOC concentration on Channel Y}) / 2) \times 100$.

APCDIFF = Absolute value of PCDIFF.

estimation of bias, using QAD as the reference. The
PCDIFF in Table 4-10 is the average of the Radian
areas for a bias term, the QAD NMOC is used to

the 95% confidence intervals for the local ambient
mean values of DIFF (from Table 4-10). Figure 4-18
Table 4-11 graphically.

RESULTS

Duplicate samples were taken during the 1990 NMOC
Duplicate samples were taken approximately every two
duplicate samples, two canisters were connected to
the of a Metal Bellows® Pump, MB151, as shown in
the orifice was gauged to deliver the appropriate
the air samples simultaneously into two canisters.
the statistics for the duplicate samples, listing sample
sampled, Julian date sampled, sample identification
the concentrations for up to three injections, the canister
the percent differences between the mean canister
the absolute percent differences.

The samples give the results for duplicate samples whose
The results of these 15 samples' analyses were used
of samples, duplicate samples, and replicate
ers are followed by "R" for the replicate analyses.
at least two injections from the canister to the
occasionally, three injections were performed in
detailed in the QAPP². Replicate analyses were
the initial analysis of a given canister. The
in ppmC, given in Column 9, is the arithmetic
ons for a given canister. These results enabled the
error, or imprecision, from sampling error (or

ated as Duplicate Percent Difference (% Diff) was
difference between the average canister

TABLE 4-11. LOCAL AMBIENT SAMPLES CONFIDENCE INTERVALS

Channel Pair (X-Y)	Mean Difference (ppmC)	Standard Deviation (ppmC)	Cases	$t_{0.975,n-1}$	95% Confidence Intervals	
					Upper	Lower
A-QAD	0.02095	0.02625	28	2.052	0.03112	0.01077
B-QAD	0.02954	0.04443	28	2.052	0.04676	0.01231
C-QAD	0.01037	0.03147	27	2.056	0.02282	-0.00208
D-QAD	0.02586	0.02224	27	2.056	0.03466	0.01706
B-A	0.00912	0.03761	30	2.045	0.02316	-0.00492
C-A	-0.01040	0.03543	29	2.048	0.00308	-0.02387
C-B	-0.02010	0.04007	29	2.048	-0.00486	-0.03534
C-D	-0.01549	0.02209	29	2.048	-0.00709	-0.02389
D-A	0.00509	0.02195	29	2.048	0.01344	-0.00326
D-B	-0.00462	0.03418	29	2.048	0.00838	-0.01761

$t_{0.975,n-1}$ = Student's t-statistic for 95% confidence interval,
where n = the number of cases in mean DIFF.

Local Ambient Samples

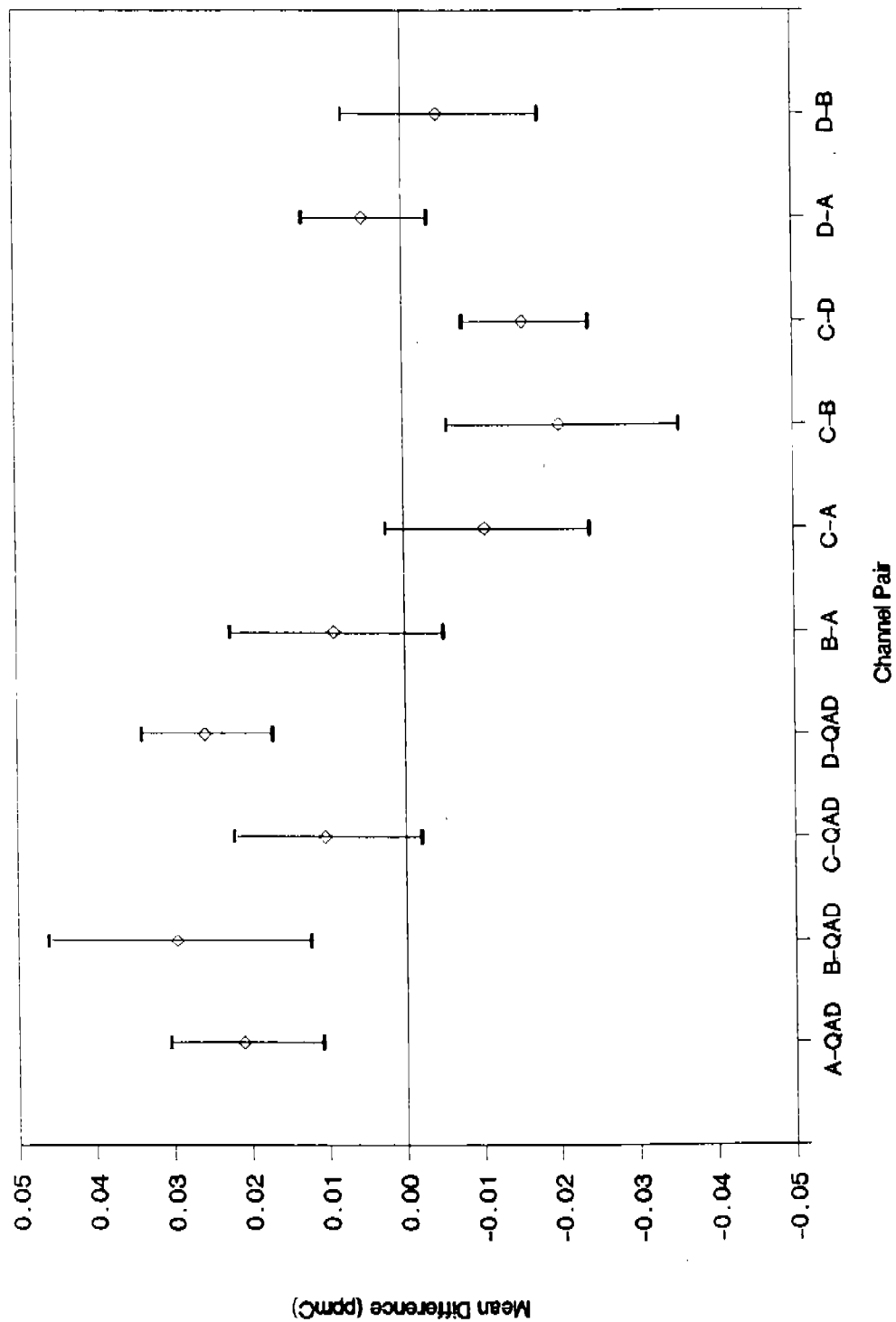


Figure 4-18. 95% Confidence intervals for mean NMOC difference.

TABLE 4-12. DUPLICATE SAMPLES FOR 1990

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj 1 NMOC (ppmC)	Inj 2 NMOC (ppmC)	Canister Mean (ppmC)	Duplicate	
								% Diff.	Abs % Diff.
1	LINY	13-Jun-90	164	1046	0.409	0.411			
	LINY	13-Jun-90	164	1046R	0.341	0.338	0.3748		
	LINY	13-Jun-90	164	1045	0.415	0.407			
2	LINY	13-Jun-90	164	1045R	0.381	0.383	0.3965	5.640	5.640
	LINY	15-Jun-90	177	1132	0.378	0.385			
	LINY	15-Jun-90	177	1132R	0.378	0.379	0.3800		
	LINY	26-Jun-90	177	1133	0.395	0.383			
	LINY	26-Jun-90	177	1133R	0.380	0.376	0.3835	0.917	0.917
3	HTCT	26-Jun-90	179	1124	0.198	0.199			
	HTCT	26-Jun-90	179	1124R	0.203	0.197	0.1993		
	HTCT	28-Jun-90	179	1125	0.245	0.263			
	HTCT	28-Jun-90	179	1125R	0.238	0.266	0.2529	23.721	23.721
4	PLNJ	28-Jun-90	180	1146	0.523	0.509			
	PLNJ	28-Jun-90	180	1146R	0.572	0.524	0.5320		
	PLNJ	29-Jun-90	180	1145	0.506	0.526			
	PLNJ	29-Jun-90	180	1145R	0.518	0.535	0.5213	-2.041	2.041
5	HTCT	29-Jun-90	208	1281	0.167	0.188			
	HTCT	29-Jun-90	208	1281R	0.152	0.179	0.1715		
	HTCT	16-Jul-90	208	1282	0.156	0.191			
	HTCT	16-Jul-90	208	1282R	0.165	0.167	0.1698	-1.026	1.026
6	BMTX	26-Jul-90	239	1453	1.429	1.510			
	BMTX	26-Jul-90	239	1453R	1.320	1.126	1.4019		
	BMTX	27-Jul-90	239	1452	1.394	1.377			
	BMTX	27-Jul-90	239	1452R	1.539	1.513	1.4556	3.770	3.770
	BMTX	27-Jul-90	240	1467	0.783	0.796			
7	BRLA	27-Jul-90	240	1467R	0.812	0.816	0.8017		
	BRLA	27-Jul-90	240	1466	0.826	0.827			
	BRLA	27-Jul-90	240	1466R	0.821	0.788	0.8155	1.703	1.703
	BRLA	27-Jul-90	240	1466R	0.821	0.788	0.8155	1.703	1.703
8	MNY	27-Aug-90	247	1495	0.473	0.468			
	MNY	27-Aug-90	247	1495R	0.583	0.459	0.4956		
	MNY	27-Aug-90	247	1494	0.554	0.541			
	MNY	27-Aug-90	247	1494R	0.484	0.523	0.5090	2.669	2.669
9	BMTX	28-Aug-90	254	1535	1.581	1.595			
	BMTX	28-Aug-90	254	1535R	0.953	0.849	1.2446		
	BMTX	28-Aug-90	254	1534	1.578	1.688			
	BMTX	28-Aug-90	254	1534R	1.644	1.619	1.6324	26.953	26.953
10	BRLA	04-Sep-90	255	1544	0.283	0.272			
	BRLA	04-Sep-90	255	1544R	0.265	0.277	0.2741		
	BRLA	04-Sep-90	255	1543	0.332	0.351			
	BRLA	04-Sep-90	255	1543R	0.431	0.448	0.3906	35.035	35.035
11	LINY	05-Sep-90	261	1572	0.234	0.258			
	LINY	05-Sep-90	261	1572R	0.301	0.294	0.2717		
	LINY	10-Sep-90	261	1571	0.150	0.352			
	LINY	10-Sep-90	261	1571R	0.352	0.301	0.2971	8.859	8.859
12	HTCT	11-Sep-90	263	1595	0.214	0.202			
	HTCT	11-Sep-90	263	1595R	0.203	0.203	0.2055		
	HTCT	11-Sep-90	263	1594	0.194	0.175			
	HTCT	11-Sep-90	263	1594R	0.191	0.205	0.1912	-7.183	7.183
13	BMTX	12-Sep-90	268	1611	2.195	2.256			
	BMTX	12-Sep-90	268	1611R	2.246	2.244	2.2519		
	BMTX	12-Sep-90	268	1610	2.242	2.000			
	BMTX	12-Sep-90	268	1610R	2.223	1.732	1.9606	-13.917	13.917
14	BRLA	18-Sep-90	271	1632	1.679	1.658			

TABLE 4-12. DUPLICATE SAMPLES FOR 1990

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj 1 NMOC (ppmC)	Inj 2 NMOC (ppmC)	Canister Mean (ppmC)	Duplicate	
								% Diff.	Abs % Diff.
15	BRLA	18-Sep-90	271	1632R	1.764	1.737	1.7094		
	BRLA	18-Sep-90	271	1631	1.798	1.682			
	BRLA	18-Sep-90	271	1631R	1.736	1.786	1.7526	2.493	2.493
	PLNJ	20-Sep-90	271	1642	2.363	2.364			
	PLNJ	20-Sep-90	271	1642R	2.415	2.404	2.3865		
	PLNJ	20-Sep-90	271	1641	2.354	2.373			
16	PLNJ	20-Sep-90	271	1641R	2.364	2.355	2.3613	-1.059	1.059
	MNY	11-Jun-90	162	1027	0.316	0.338	0.3270		
17	MNY	11-Jun-90	162	1026	0.384	0.380	0.3820	15.515	15.515
	HTCT	13-Jun-90	164	1047	0.290	0.262	0.2760		
18	HTCT	13-Jun-90	164	1048	0.220	0.251	0.2355	-15.836	15.836
	NWNJ	14-Jun-90	165	1062	1.188	1.192	1.1900		
19	NWNJ	14-Jun-90	165	1061	1.034	1.034	1.0340	-14.029	14.029
	PLNJ	15-Jun-90	166	1066	0.419	0.378	0.3985		
20	PLNJ	15-Jun-90	166	1065	0.365	0.392	0.3777	-5.397	5.397
	NWNJ	28-Jun-90	179	1128	0.269	0.276	0.2725		
21	NWNJ	28-Jun-90	179	1129	0.239	0.248	0.2435	-11.240	11.240
	BMTX	02-Jul-90	183	1140	1.398	1.336	1.3670		
22	BMTX	02-Jul-90	183	1141	1.510	1.600	1.5550	12.868	12.868
	BRLA	05-Jul-90	186	1160	0.309	0.317	0.3130		
23	BRLA	05-Jul-90	186	1159	0.331	0.309	0.3200	2.212	2.212
	BMTX	09-Jul-90	190	1171	2.130	2.080	2.1050		
24	BMTX	09-Jul-90	190	1163	2.090	2.140	2.1150	0.474	0.474
	MNY	09-Jul-90	190	1180	0.345	0.356	0.3505		
25	MNY	09-Jul-90	190	1178	0.387	0.370	0.3785	7.682	7.682
	LINY	10-Jul-90	191	1188	0.336	0.305	0.3205		
26	LINY	10-Jul-90	191	1187	0.356	0.353	0.3545	10.074	10.074
	HTCT	11-Jul-90	192	1190	0.275	0.276	0.2755		
27	HTCT	11-Jul-90	192	1189	0.256	0.253	0.2545	-7.925	7.925
	NWNJ	12-Jul-90	193	1205	0.415	0.454	0.4345		
28	NWNJ	12-Jul-90	193	1204	0.487	0.524	0.5055	15.106	15.106
	PLNJ	13-Jul-90	194	1219	0.206	0.182	0.1940		
29	PLNJ	13-Jul-90	194	1220	0.176	0.175	0.1755	-10.014	10.014
	BMTX	16-Jul-90	197	1214	0.947	0.925	0.9360		
30	BMTX	16-Jul-90	197	1215	0.952	1.302	1.1270	18.517	18.517
	BRLA	17-Jul-90	198	1224	0.278	0.279	0.2785		
31	BRLA	17-Jul-90	198	1223	0.377	0.277	0.3270	16.020	16.020
	MNY	23-Jul-90	204	1259	0.417	0.395	0.4060		
32	MNY	23-Jul-90	204	1258	0.378	0.442	0.4417	8.345	8.345
	LINY	24-Jul-90	205	1271	0.345	0.331	0.3380		
33	LINY	24-Jul-90	205	1270	0.287	0.282	0.2845	-17.189	17.189
	NWNJ	26-Jul-90	207	1285	0.170	0.169	0.1695		
34	NWNJ	26-Jul-90	207	1286	0.234	0.204	0.2190	25.483	25.483
	PLNJ	27-Jul-90	208	1293	0.279	0.294	0.2865		
35	PLNJ	27-Jul-90	208	1292	0.268	0.311	0.2895	1.042	1.042
	BMTX	30-Jul-90	211	1302	1.990	2.071	2.0305		
36	BMTX	30-Jul-90	211	1301	2.128	2.204	2.1660	6.458	6.458
	BRLA	31-Jul-90	212	1310	0.740	0.739	0.7395		
37	BRLA	31-Jul-90	212	1309	0.745	0.787	0.7660	3.520	3.520
	LINY	07-Aug-90	219	1364	0.252	0.233	0.2425		
38	LINY	07-Aug-90	219	1359	0.342	0.297	0.3195	27.402	27.402
	NWNJ	09-Aug-90	221	1385	0.220	0.224	0.2220		
38	NWNJ	09-Aug-90	221	1370	0.200	0.203	0.2016	-9.609	9.609

TABLE 4-12. DUPLICATE SAMPLES FOR 1990

Sample No.	Site Code	Date Sampled	Julian Date Sampled	Sample ID Number	Inj 1 NMOC (ppmC)	Inj 2 NMOC (ppmC)	Canister Mean (ppmC)	Duplicate	
								% Diff.	Abs % Diff.
39	PLNJ	10-Aug-90	222	1377	0.448	0.460	0.4540		
	PLNJ	10-Aug-90	222	1375	0.475	0.453	0.4640	2.179	2.179
40	BRLA	14-Aug-90	226	1386	0.512	0.501	0.5065		
	BRLA	14-Aug-90	226	1387	0.504	0.504	0.5040	-0.495	0.495
41	BMTX	14-Aug-90	226	1388	1.366	1.406	1.3860		
	BMTX	14-Aug-90	226	1389	1.507	1.549	1.5280	9.746	9.746
42	MNY	20-Aug-90	232	1418	0.250	0.250	0.2503		
	MNY	20-Aug-90	232	1417	0.333	0.302	0.3175	23.690	23.690
43	HTCT	22-Aug-90	234	1428	0.249	0.179	0.2140		
	HTCT	22-Aug-90	234	1424	0.172	0.165	0.1685	-23.791	23.791
44	NWNJ	23-Aug-90	235	1435	0.389	0.255	0.3200		
	NWNJ	23-Aug-90	235	1434	0.404	0.419	0.4114	25.644	25.644
45	PLNJ	24-Aug-90	236	1451	0.153	0.175	0.1641		
	PLNJ	24-Aug-90	236	1450	0.287	0.307	0.2970	57.617	57.617
46	LINY	21-Aug-90	233	1456	0.091	0.084	0.0875		
	LINY	21-Aug-90	233	1426	0.074	0.045	0.0595	-38.095	38.095
47	LINY	05-Sep-90	248	1504	1.352	1.433	1.3924		
	LINY	05-Sep-90	248	1503	1.355	1.387	1.3712	-1.530	1.530
48	HTCT	06-Sep-90	249	1512	0.434	0.444	0.4390		
	HTCT	06-Sep-90	249	1511	0.498	0.518	0.5084	14.656	14.656
49	NWNJ	07-Sep-90	250	1522	0.605	0.532	0.5685		
	NWNJ	07-Sep-90	250	1521	0.520	0.541	0.5305	-6.915	6.915
50	PLNJ	10-Sep-90	253	1524	0.228	0.200	0.2140		
	PLNJ	10-Sep-90	253	1523	0.261	0.243	0.2520	16.309	16.309
51	MNY	18-Sep-90	261	1580	0.420	0.434	0.4270		
	MNY	18-Sep-90	261	1579	0.419	0.404	0.4113	-3.746	3.746
52	BRLA	25-Sep-90	268	1616	0.280	0.238	0.2589		
	BRLA	25-Sep-90	268	1613	0.430	0.438	0.4343	50.603	50.603
53	BRLA	26-Sep-90	269	1621	1.385	1.341	1.3628		
	BRLA	26-Sep-90	269	1620	1.288	1.304	1.2958	-5.040	5.040
54	NWNJ	21-Sep-90	264	1601	0.651	0.672	0.6615		
	NWNJ	21-Sep-90	264	1602	0.681	0.672	0.6765	2.242	2.242
55	NWNJ	26-Sep-90	269	1629	0.224	0.197	0.2106		
	NWNJ	26-Sep-90	269	1630	0.559	0.533	0.5460	88.649	88.649
56	HTCT	27-Sep-90	270	1634	0.400	0.382	0.3910		
	HTCT	27-Sep-90	270	1633	0.484	0.490	0.4870	21.868	21.868
57	NWNJ	27-Sep-90	270	1622	0.753	0.696	0.7275		
	NWNJ	27-Sep-90	270	1623	0.807	0.809	0.8079	10.584	10.584
58	PLNJ	27-Sep-90	270	1624	1.193	1.231	1.1891		
	PLNJ	27-Sep-90	270	1625	0.991	1.109	1.0924	-8.472	8.472
59	NWNJ	28-Sep-90	271	1643	1.940	2.130	2.0350		
	NWNJ	28-Sep-90	271	1644	2.041	2.050	2.0455	0.515	0.515

concentrations ($\text{NMOC}_2 - \text{NMOC}_1$), dividing by the average of the two canister concentrations, and multiplying by 100. The choice of which duplicate was designated No. 1 and which was designated No. 2 was arbitrary, and thus the overall average percent difference was near zero and equaled 6.82 percent. Duplicate percent difference ranged from -37.91 to 88.65 percent. The duplicate percent difference range and overall average compare favorably with the percent difference range and average in the 1989 Final Report³ of from -80.51 to 71.54, averaging 4.24 percent. Absolute percent difference disregarded the sign of the percent difference previously calculated and averaged 13.75%, which compares favorably with results from previous years in the NMOC Monitoring Program.³ The range for duplicate differences in 1989 was -80.52 to +71.55 percent. Absolute percent difference in 1989 averaged 14.19 percent.

Measured NMOC concentrations for duplicate canister samples provide the data used to estimate an overall sampling and analytical error. Sampling error includes differences caused by any residual organic compounds in the canisters after cleaning and before sampling. Sampling error also involves differences caused by drawing the ambient air sample into the canister, and differences between the analysis of the two canisters caused by removing the sample from the canister when it is introduced into the analytical device. Analytical error is measured from replicate analyses from the same canister. In the protocol used in the 1990 NMOC Monitoring Program, replicate analyses are performed as follows.

Each analysis involved at least two aliquots taken from a canister. The first analysis was performed on the same day the canister was received from the site. The second, or replicate analysis, also involved at least two aliquots taken from the same canister, but the second analysis was performed at least one day after the first analysis. The time interval between the first and the second analysis allowed the contents of the canister to re-establish equilibrium between the sample and the solid surfaces of the canister. For each analysis, if the standard deviation between the first and the second injection was greater than 0.030 ppmC, then a third injection was performed.

In the following section, analytical error, or precision, is estimated from replicate analyses. In subsequent sections, components of the error (or precision) are examined to determine what fraction of the total precision (or imprecision) is attributable to sampling, and what fraction results from analytical imprecision.

4.5.1 Analytical Precision

Analytical precision is estimated from replicate analyses. Table 4-13 summarizes the replicate analysis results for the 1990 NMOC Monitoring Program. The first 15 samples listed in Table 4-13 show results in which the analyses of duplicate samples were replicated. As shown in the table, the overall average precision in terms of average percent difference was -1.36. In terms of average absolute percent difference, the analytical precision was 7.59. These figures compare with the duplicate precisions discussed in the previous section of 6.34% difference, and 12.33 absolute percent difference. The duplicate imprecision statistics are expected to be greater than the analytical imprecision statistics, because the duplicate precision includes both sampling and analytical error. The range for the analytical precision was from -55.17 to 25.11 with a standard deviation for percent difference equal to 12.79. For the replicate analyses, percent difference was calculated from the following:

$$\text{Percent difference} = (\text{NMOC}_2 - \text{NMOC}_1) / ((\text{NMOC}_2 + \text{NMOC}_1) / 2), \quad (1)$$

where:

NMOC₁ is the mean concentration in ppmC from the first analysis, and
 NMOC₂ is the mean concentration in ppmC of the second, or replicate analysis.

4.5.2 Components of Variance

All of the duplicate samples (see Table 4-12) were subjected to an analysis of variance (ANOVA) to separate the sampling variability from the analytical variability. Equation 2 gives the model for this ANOVA.

$$\text{NMOC}_{ijk} = \mu + S_i + D_{j(i)} + \epsilon_{k(ij)}, \quad (2)$$

TABLE 4-13. REPLICATE ANALYSES FOR THE 1990 NMOC MONITORING PROGRAM

Sample No.	Site Code	Julian Date Sampled	Date Sampled	Sample ID No.	Inj 1 NMOC (ppmC)	Inj 2 NMOC (ppmC)	Inj 3 NMOC (ppmC)	Mean NMOC (ppmC)	Radiation Channel	Canister Mean (ppmC)	Replicate	
											% Diff.	Abs. % Diff.
1	LINY	164	13-Jun-90	1046	0.409	0.411		0.4100	B			
	LINY	164	13-Jun-90	1046R	0.341	0.338		0.3395	C	0.3748	-18.813	18.813
	LINY	164	13-Jun-90	1045	0.415	0.407		0.4110	A			
2	LINY	164	13-Jun-90	1045R	0.381	0.383		0.3820	C	0.3965	-7.314	7.314
	LINY	177	15-Jun-90	1132	0.378	0.385		0.3815	C			
	LINY	177	15-Jun-90	1132R	0.378	0.379		0.3785	B	0.3800	-0.789	0.789
3	LINY	177	26-Jun-90	1133	0.395	0.383		0.3890	D	0.3835	-2.868	2.868
	LINY	177	26-Jun-90	1133R	0.380	0.376		0.3780	A			
	HTCT	179	26-Jun-90	1124	0.198	0.199		0.1985	B			
4	HTCT	179	26-Jun-90	1124R	0.203	0.197		0.2000	D	0.1993	0.753	0.753
	HTCT	179	28-Jun-90	1125	0.245	0.263		0.2538	A			
	HTCT	179	28-Jun-90	1125R	0.238	0.266		0.2520	C	0.2529	-0.692	0.692
5	PLNJ	180	28-Jun-90	1146	0.523	0.509		0.5160	A			
	PLNJ	180	28-Jun-90	1146R	0.572	0.524		0.5480	A	0.5320	6.015	6.015
	PLNJ	180	29-Jun-90	1145	0.506	0.526		0.5160	B			
6	PLNJ	180	29-Jun-90	1145R	0.518	0.535		0.5265	B	0.5213	2.014	2.014
	HTCT	208	29-Jun-90	1281	0.167	0.188		0.1775	A			
	HTCT	208	29-Jun-90	1281R	0.152	0.179		0.1655	D	0.1715	-6.997	6.997
7	HTCT	208	16-Jul-90	1282	0.156	0.191		0.1735	C			
	HTCT	208	16-Jul-90	1282R	0.165	0.167		0.1660	C	0.1698	-4.418	4.418
	BMTX	239	26-Jul-90	1453	1.429	1.510	1.557	1.4695	D	1.4019	-9.652	9.652
8	BMTX	239	26-Jul-90	1453R	1.320	1.126		1.3342	D			
	BMTX	239	27-Jul-90	1452	1.394	1.377		1.3855	C	1.4556	9.632	9.632
	BMTX	239	27-Jul-90	1452R	1.539	1.513		1.5257	B			
9	BRLA	240	27-Jul-90	1467	0.783	0.796		0.7894	B	0.8017	3.071	3.071
	BRLA	240	27-Jul-90	1467R	0.812	0.816		0.8140	A			
	BRLA	240	27-Jul-90	1466	0.826	0.827		0.8265	A	0.8155	-2.692	2.692
10	BRLA	240	27-Jul-90	1466R	0.821	0.788		0.8045	B			
	MNY	247	27-Aug-90	1495	0.473	0.468		0.4702	D	0.4956	10.215	10.215
	MNY	247	27-Aug-90	1495R	0.583	0.459		0.5209	C			
11	MNY	247	27-Aug-90	1494	0.554	0.541		0.5473	C			
	MNY	247	27-Aug-90	1494R	0.484	0.523	0.405	0.4707	D	0.5090	-15.057	15.057
	BMTX	254	28-Aug-90	1535	1.581	1.595		1.5880	D			
12	BMTX	254	28-Aug-90	1535R	0.953	0.849		0.9013	A	1.2446	-55.171	55.171
	BMTX	254	28-Aug-90	1534	1.578	1.688		1.6331	C			
	BMTX	254	28-Aug-90	1534R	1.644	1.619		1.6317	D	1.6324	-0.087	0.087
13	BRLA	255	04-Sep-90	1544	0.283	0.272		0.2772	B			
	BRLA	255	04-Sep-90	1544R	0.265	0.277		0.2711	B	0.2741	-2.229	2.229
	BRLA	255	04-Sep-90	1543	0.332	0.351		0.3415	A			

TABLE 4-13. CONTINUED

Sample No.	Site Code	Julian Date Sampled	Date Sampled	Sample ID No.	Inj 1 NMOC (ppmC)	Inj 2 NMOC (ppmC)	Inj 3 NMOC (ppmC)	Mean NMOC (ppmC)	Radian Inst Channel	Canister Mean (ppmC)	Replicate	
											% Diff.	Abs. % Diff.
11	BRLA	255	04-Sep-90	1543R	0.431	0.448		0.4396	A	0.3906	25.111	25.111
	LINY	261	05-Sep-90	1572	0.234	0.258		0.2461	C			
	LINY	261	05-Sep-90	1572R	0.301	0.294		0.2973	D	0.2717	18.842	18.842
	LINY	261	10-Sep-90	1571	0.150	0.352	0.301	0.2677	D			
12	LINY	261	10-Sep-90	1571R	0.352	0.301		0.3264	D	0.2971	19.738	19.738
	HTCT	263	11-Sep-90	1595	0.214	0.202		0.2080	D			
	HTCT	263	11-Sep-90	1595R	0.203	0.203		0.2030	C	0.2055	-2.460	2.460
	HTCT	263	11-Sep-90	1594	0.194	0.175		0.1847	C			
13	HTCT	263	11-Sep-90	1594R	0.191	0.205		0.1978	D	0.1912	6.875	6.875
	HTCT	263	11-Sep-90	1594R	0.191	0.205		0.1978	D			
	BMTX	268	12-Sep-90	1611	2.195	2.256	2.325	2.2587	D	2.2519	-0.605	0.605
	BMTX	268	12-Sep-90	1611R	2.246	2.244		2.2450	D			
14	BMTX	268	12-Sep-90	1610	2.242	2.000	1.596	1.9459	A	1.9606	1.493	1.493
	BMTX	268	12-Sep-90	1610R	2.223	1.732	1.971	1.9752	A			
	BMTX	268	12-Sep-90	1610R	2.223	1.732		1.6686	B			
	BMTX	268	12-Sep-90	1610R	2.223	1.732		1.7503	B	1.7094	4.782	4.782
15	BRLA	271	18-Sep-90	1632	1.679	1.658		1.6686	B			
	BRLA	271	18-Sep-90	1632R	1.764	1.737		1.7503	B			
	BRLA	271	18-Sep-90	1631	1.798	1.682	1.752	1.7442	A	1.7526	0.964	0.964
	BRLA	271	18-Sep-90	1631R	1.736	1.786		1.7611	A			
16	PLNJ	271	20-Sep-90	1642	2.363	2.364		2.3635	C	2.3865	1.927	1.927
	PLNJ	271	20-Sep-90	1642R	2.415	2.404		2.4095	C			
	PLNJ	271	20-Sep-90	1641	2.354	2.373		2.3635	D	2.3613	-0.182	0.182
	PLNJ	271	20-Sep-90	1641R	2.364	2.355		2.3592	D			
17	PLNJ	271	20-Sep-90	1641R	2.364	2.355		2.3592	D			
	PLNJ	271	20-Sep-90	1641R	2.364	2.355		2.3592	D			
	PLNJ	271	20-Sep-90	1641R	2.364	2.355		2.3592	D			
	PLNJ	271	20-Sep-90	1641R	2.364	2.355		2.3592	D			
18	PLNJ	166	25-Sep-90	1066	0.419	0.378		0.3990	B	0.3825	-8.627	8.627
	PLNJ	166	25-Sep-90	1066R	0.356	0.376		0.3660	B			
	PLNJ	166	25-Sep-90	1066R	0.356	0.376		0.3660	B			
	PLNJ	166	25-Sep-90	1066R	0.356	0.376		0.3660	B			
19	BMTX	197	25-Sep-90	1215	0.952	1.302		1.1300	B	1.1305	0.088	0.088
	BMTX	197	25-Sep-90	1215R	1.141	1.122		1.1310	B			
	BMTX	197	25-Sep-90	1215R	1.141	1.122		1.1310	B			
	BMTX	197	25-Sep-90	1215R	1.141	1.122		1.1310	B			
20	NWNJ	207	27-Sep-90	1285	0.170	0.169		0.1690	C	0.1650	-4.848	4.848
	NWNJ	207	27-Sep-90	1285R	0.169	0.152		0.1610	C			
	NWNJ	207	27-Sep-90	1285R	0.169	0.152		0.1610	C			
	NWNJ	207	27-Sep-90	1285R	0.169	0.152		0.1610	C			
21	PLNJ	208	28-Sep-90	1293	0.279	0.294		0.2860	C	0.2905	3.098	3.098
	PLNJ	208	28-Sep-90	1293R	0.287	0.303		0.2950	D			
	PLNJ	208	28-Sep-90	1293R	0.287	0.303		0.2950	D			
	PLNJ	208	28-Sep-90	1293R	0.287	0.303		0.2950	D			
22	LINY	248	28-Sep-90	1503	1.355	1.387	1.443	1.3712	D	1.3767	0.792	0.792
	LINY	248	28-Sep-90	1503R	1.387	1.317		1.3821	C			
	LINY	248	28-Sep-90	1503R	1.387	1.317		1.3821	C			
	LINY	248	28-Sep-90	1503R	1.387	1.317		1.3821	C			
23	PLNJ	253	28-Sep-90	1524	0.228	0.200		0.2140	B	0.1988	-15.346	15.346
	PLNJ	253	28-Sep-90	1524R	0.196	0.171		0.1835	B			
	PLNJ	253	28-Sep-90	1524R	0.196	0.171		0.1835	B			
	PLNJ	253	28-Sep-90	1524R	0.196	0.171		0.1835	B			
24	NWNJ	270	28-Sep-90	1623	0.807	0.809		0.8077	B	0.7815	-6.705	6.705
	NWNJ	270	28-Sep-90	1623R	0.807	0.809		0.8077	B			
	NWNJ	270	28-Sep-90	1623R	0.807	0.809		0.8077	B			
	NWNJ	270	28-Sep-90	1623R	0.807	0.809		0.8077	B			
Average											-1.3553	7.5936

where:

- NMOC_{ijk} = NMOC concentration from sample injection ijk ;
- μ = overall mean concentration in ppmC;
- S_i = effect of sample on NMOC_i , $i = 1, 2, \dots, a$;
- $D_{j(0)}$ = pooled duplicate effect, $j = 1, \dots, b$; and
- $\epsilon_{k(ij)}$ = residual, taken to be the analytical error.

The duplicate effects are nested within samples, and $D_{j(0)}$ represents the pooled duplicate effect of all the duplicates. As shown in Table 4-12, 59 pairs of duplicate samples were included in the 1990 NMOC Monitoring Program. It was necessary to break the duplicate samples into two subgroups to process the results. These results are shown in Tables 4-14 and 4-15. For each case, the nested duplicate effect is highly significant, as testified by the value of P in the ANOVA table for $D_{j(k)}$ being less than 0.010. It is therefore possible to separate the sampling variance from the analytical variance. In each ANOVA table, the figure under the column titled Mean Square and in the row for $D_{j(0)}$ is the pooled variance for $D_{j(0)}$. Equation 3 shows how this variance is apportioned between the sampling variance σ_d^2 and the analytical variance σ_ϵ^2 .

$$\text{Pooled variance for } D_{j(0)} = \sigma_\epsilon^2 + a(b-1)\sigma_d^2, \quad (3)$$

where:

σ_ϵ^2 is shown in the ANOVA table in the row containing $\epsilon_{k(ij)}$ and listed under the Mean Square column. For example for the ANOVA in Table 4-14, and using Equation 3,

$$0.039591 = 0.010940 + 15 \sigma_d^2, \quad (4)$$

$$\text{from which } \sigma_d^2 = 0.001910. \quad (5)$$

The total variance, or variability, for the PDFID method of measuring NMOC is

$$\sigma^2 = \sigma_d^2 + \sigma_\epsilon^2. \quad (6)$$

TABLE 4-14. ANOVA FOR DUPLICATE SAMPLES 1 THROUGH 15

Source	Sum of Squares	df	Mean Square	F Ratio	P
S_1	0.687146	14	4.908183	0.448663	0.999201E-15
$D_{(0)}$	0.593862	15	0.039591	3.618921	0.000056
$\epsilon_{K(0)}$	1.061139	97	0.010940		

TABLE 4-15. ANOVA FOR DUPLICATE SAMPLES 16 THROUGH 59

Source	Sum of Squares	df	Mean Square	F Ratio	P
S_i	0.513211	43	1.193515	0.684027E+03	0.999201E-15
$D_{j(i)}$	0.391607	44	0.008900	5.100857	0.159790E-10
$\epsilon_{k(ij)}$	0.165758	95	0.001745		

Thus for the data included in Table 4-14, the total variance, sampling plus analytical error, may be estimated

$$\sigma^2 = 0.010940 + 0.001910, \text{ or} \quad (7)$$

$$\sigma^2 = 0.012850. \quad (8)$$

The percent of the total variability due to analysis is:

$$\sigma_e^2 / \sigma^2 \cdot 100 = (0.010940 / 0.01285)100 \quad (9)$$

$$\text{Analytical variability} = 85.14\%. \quad (10)$$

Similarly sampling variability is calculated as follows:

$$\text{Sampling variability} = (0.001910 / 0.012850)100 \quad (11)$$

$$\text{Sampling variability} = 14.86\%. \quad (12)$$

Standard deviations (or precisions) for analysis, s_e , sampling, s_d , and total error, s , may be calculated from the positive square roots of the corresponding variances:

$s_e = 0.1046$ ppmC, a pooled standard deviation for analysis;

$s_d = 0.0437$ ppmC, a pooled standard deviation for sampling; and

$s = 0.1134$ ppmC, a pooled standard deviation for the total NMOC measurement process.

These statistics, derived for the duplicate pairs analyzed in Table 4-14, are summarized in Table 4-16, which also shows the mean NMOC concentration for each subset, and estimates of the percent coefficients of variation.

As seen from Table 4-16, the analytical component of the variability ranges from about 85% to 91%, leaving the sampling variability to range from 15% to about 9 percent.

TABLE 4-16. COMPONENTS OF VARIANCE, NMOC SAMPLING AND ANALYSIS

N	No. Sample	Variance		Total		% of Variability		Standard Deviation (ppmC)		\bar{X} (ppmC)	% Coefficient of Variation	
		Analysis	Sampling	Analysis	Sampling	Analysis	Sampling	Analysis	Sampling		Analysis	Sampling
127	15	0.01094	0.001910	0.012850	14.66	0.1046	0.0437	0.1134	0.6910	11.7	4.90	12.7
183	44	0.001745	0.000163	0.001907	8.53	0.0418	0.0128	0.0437	0.5788	7.22	2.21	7.55

4.6 CANISTER PRESSURE RESULTS

Canister pressure results for the NMOC Monitoring Program are important to be sure that the ambient air samples obtained are representative. The NMOC sampling systems are designed to obtain an integrated ambient air sample between 6:00 a.m. and 9:00 a.m., or at other programmed intervals. Canister pressures are being measured to obtain a better understanding of the range and magnitude of pressures being generated by the NMOC sampling systems. Canister pressure data are given in Tables 4-17 and 4-18 for both single canister samples and duplicate samples. The pressures reported in Tables 4-17 and 4-18 are the canister sampling pressures measured immediately before analysis in the laboratory. A significant decrease between the field sampling pressure and the laboratory value might indicate a leak. The canister was leak tested when this occurred.

Table 4-17 gives statistics for single and duplicate samples. All sample canisters averaged 15.3 psig, while duplicate samples averaged 16.4 psig. The column entitled "All Samples" includes pressures from both single samples and duplicate samples. Standard deviations were 3.4 and 3.0 psig, respectively.

4.7 CANISTER CLEANUP RESULTS

Prior to the start of the 1990 NMOC Sampling and Analysis Program all of the canisters were cleaned and analyzed for their NMOC content to establish canister initial conditions. The resulting analysis with cleaned, dried air that had been humidified averaged 3.2 area counts (0.0010 ppmC), ranging from zero to 40.63 area counts (0.012 ppmC). Any canisters that produced more than 0.025 ppmC were recleaned.

Continual monitoring of the cleanup was important to ensure that there was negligible carryover from one site sample to the next. The daily canister cleanup procedure is described in detail in Section 3.4. The NMOC content was below 0.020 ppmC and cleanup was considered to be satisfactory.

Average percent recoveries, or average percent cleanup, in 1990 averaged 99.747% (99.742% in 1989, 99.689% in 1988, 99.374% in 1987, 99.881% in 1986, and 99.898% in 1985), ranging from 92.12% to 100 percent. The reported average percent recovery is based on average NMOC concentration and average cleanup concentration. The reported percent cleanup figures should be considered minimum values. The actual percent cleanup was greater than the

TABLE 4-17. NMOC PRESSURE STATISTICS

Statistics	All Samples	Duplicate Sample Canisters
Number of Cases	536	114
Minimum Pressure, psig	6.0	10.0
Maximum Pressure, psig	36.0	30.0
Mean Pressure, psig	15.3	16.4
Median Pressure, psig	14.5	17.0
Standard Deviation, psig	3.4	3.0
Skewness	1.47	1.43
Kurtosis	5.67	6.14

TABLE 4-18. PRESSURE DISTRIBUTION OF NMOC AMBIENT AIR SAMPLES

Pressure Range, psig	Single Sample Cases	Duplicate Sample Canister Cases ^b
Blank ^a	8	0
6.0 to 6.9	1	0
7.0 to 7.0	2	0
8.0 to 8.9	2	0
9.0 to 9.9	3	0
10.0 to 10.9	4	4
11.0 to 11.9	52	2
12.0 to 12.9	39	0
13.0 to 13.9	61	10
14.0 to 14.9	89	16
15.0 to 15.9	29	12
16.0 to 16.9	26	12
17.0 to 17.9	64	24
18.0 to 18.9	63	20
19.0 to 19.9	14	10
20.0 to 20.9	7	0
21.0 to 21.9	1	0
22.0 to 22.9	2	0
23.0 to 23.9	0	2
24.0 to 24.9	0	0
25.0 to 25.9	1	0
26.0 to 26.9	1	0
27.0 to 27.9	1	0
28.0 to 28.9	2	0
29.0 to 29.9	0	0
30.0 to 36.0	5	2
Total	477	114

^aBlank indicates no pressure reading given for sample.

^bEquals 57 duplicate samples.

reported values because, after the percent cleanup was measured, the canister was evacuated a third time before being shipped to the site.

4.8 EXTERNAL AUDIT RESULTS

Primary measures of accuracy were calculated from the results of the analysis of audit samples provided by EPA-QAD. Results are reported in terms of percent bias, relative to the EPA standards.

Audit samples of propane provided by EPA-QAD were referenced to NIST propane CRM No. 1668B. Each Radian channel analyzed each audit sample. The results of these analyses are given in Table 4-19. Audit sample bias, percent bias, and absolute percent bias are shown in Table 4-20. In Table 4-20, all bias measurements are relative to the QAD results. Overall Radian average bias was 1.07%, indicating Radian channels averaged 1.07% higher than the EPA-QAD reference values. Radian mean bias ranged from -3.18% for Channel D to 6.23% for Channel A. The overall average absolute percent bias for the Radian channels was 5.04 percent. These accuracy measurements show excellent agreement with the reference values, and lend absolute percent bias for the Radian channels was 5.04 percent. These accuracy measurements show excellent agreement with the reference values, and lend confidence to the 1990 NMOC concentration results determined on all the Radian channels.

Figures 4-19, 4-20, 4-21, and 4-22 show the audit bias results for the Radian channels versus the reference values provided by EPA-QAD.

4.9 DATA VALIDATION

The secondary backup disks were updated daily on 20 megabyte hard disks. At the completion of the sampling and analysis phase 100% of the data base was checked to verify its validity. Items checked included original data sheets, checks of all the calculations, and data transfers. In making the calculations for the final report and other reports, corrections were made to the data base as errors or omissions were encountered.

A total of 780 NMOC concentration measurements were performed by Radian in June through September 1990. For the regular 1990 NMOC Monitoring Program, there were 613 NMOC concentration measurements which included 593 sample analyses, 37 repeated analyses, 26 local ambient samples (x 4 analyses each with the exception of two samples for which only two analyses each were performed), and 4 audit samples (x 4 analyses each). The remaining 12 analyses included analyses from the 1990 Portland Monitoring Program.

TABLE 4-19. 1990 NMOC AUDIT SAMPLE RESULTS

Analyzed Date	Julian Date	Radian ID Number	Channel				QAD NMOC ppmC
			A NMOC ppmC	B NMOC ppmC	C NMOC ppmC	D NMOC ppmC	
6/20/90	171	1053	2.330	2.249	2.271	2.174	2.280
6/20/90	171	1054	1.003	0.974	0.962	0.975	0.936
6/20/90	171	1073	0.715	0.678	0.678	0.669	0.647
6/20/90	171	1074	1.930	1.673	1.822	1.550	1.837

AUDIT BIAS

Radian Channel A vs. QAD

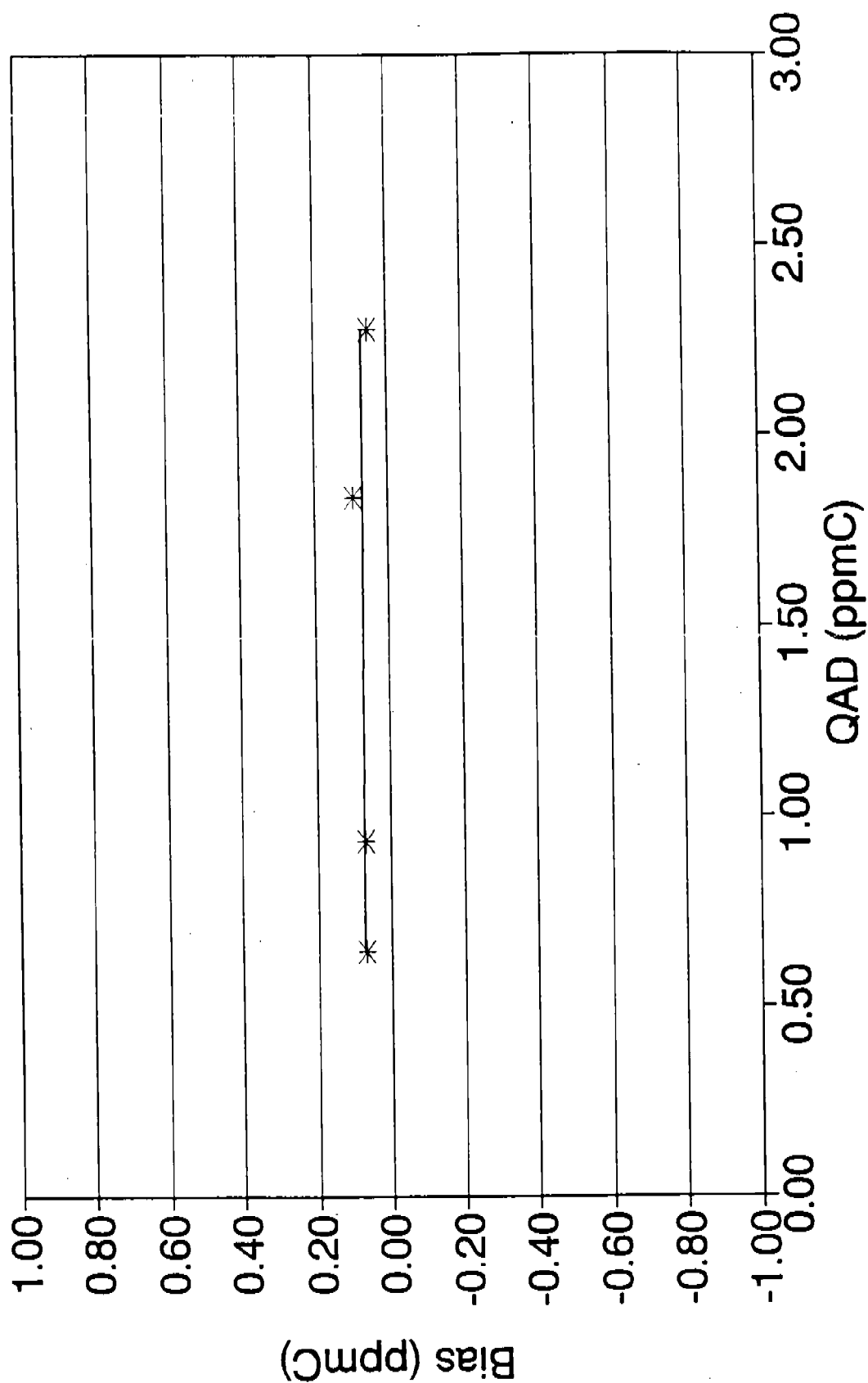


Figure 4-19. Audit bias, Radian Channel A vs. EPA-QAD.

AUDIT BIAS

Radian Channel B vs. QAD

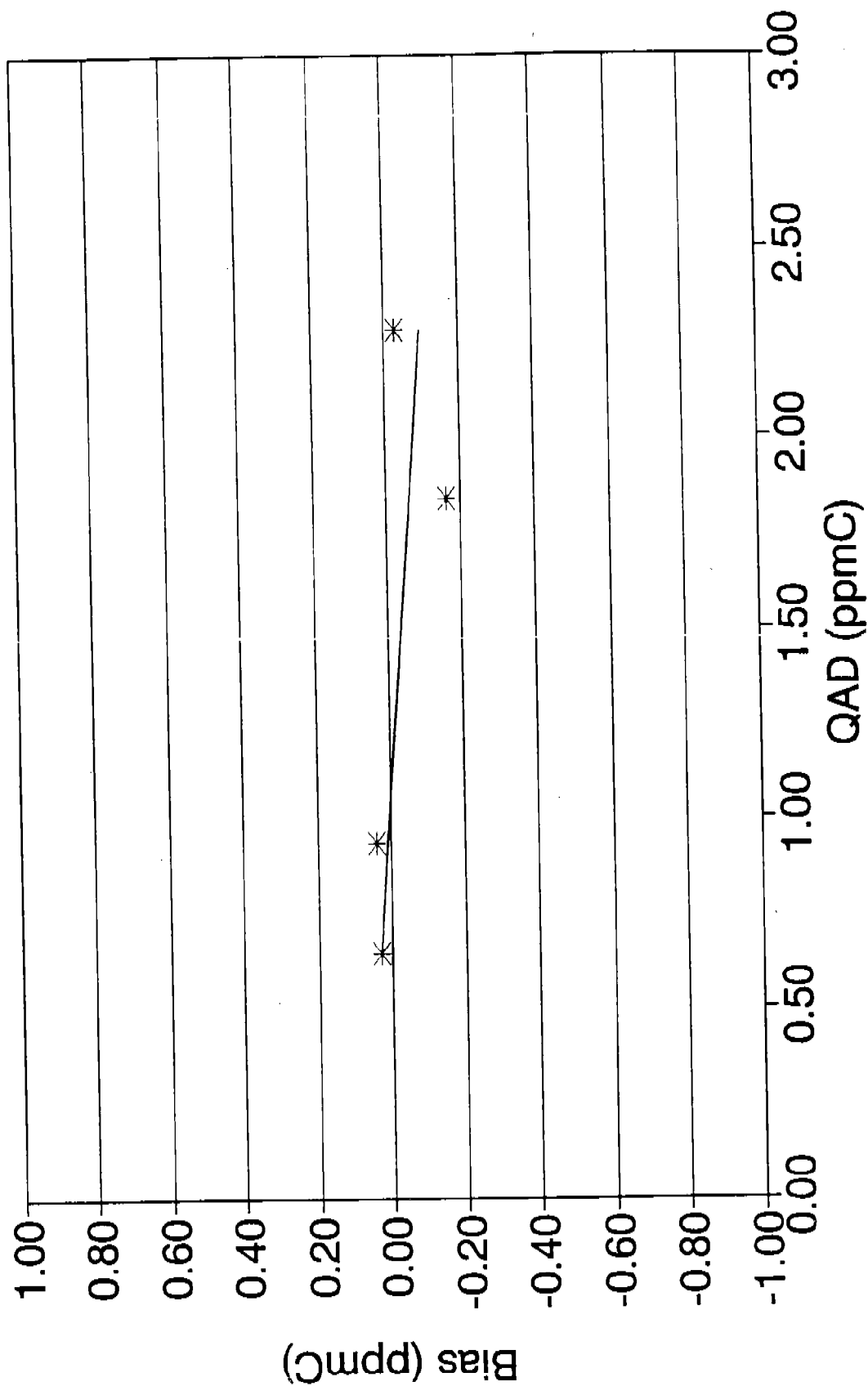


Figure 4-20. Audit bias, Radian Channel B vs. EPA-QAD.

AUDIT BIAS

Radian Channel C vs. QAD

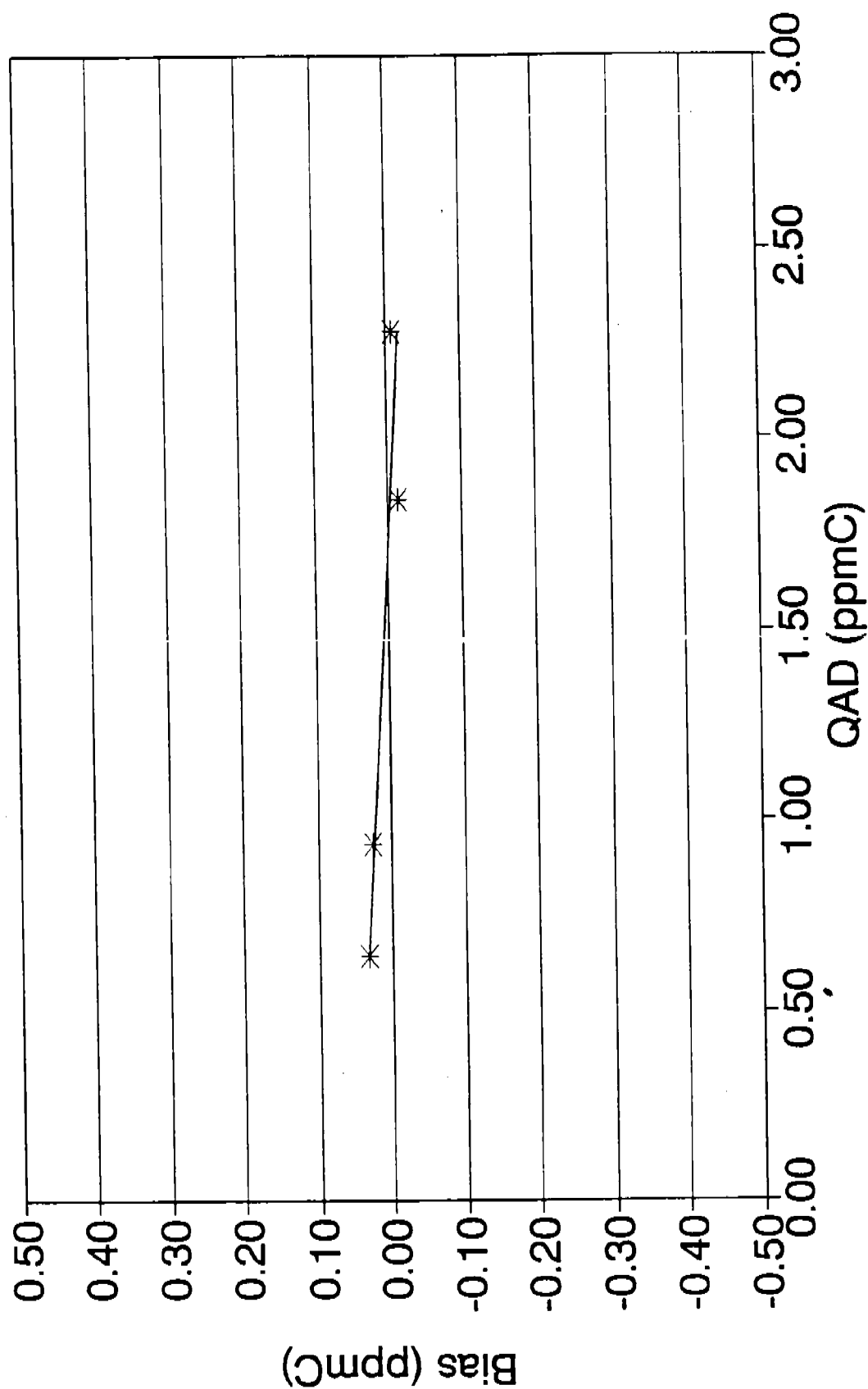


Figure 4-21. Audit bias, Radian Channel C vs. EPA-QAD.

AUDIT BIAS

Radian Channel D vs. QAD

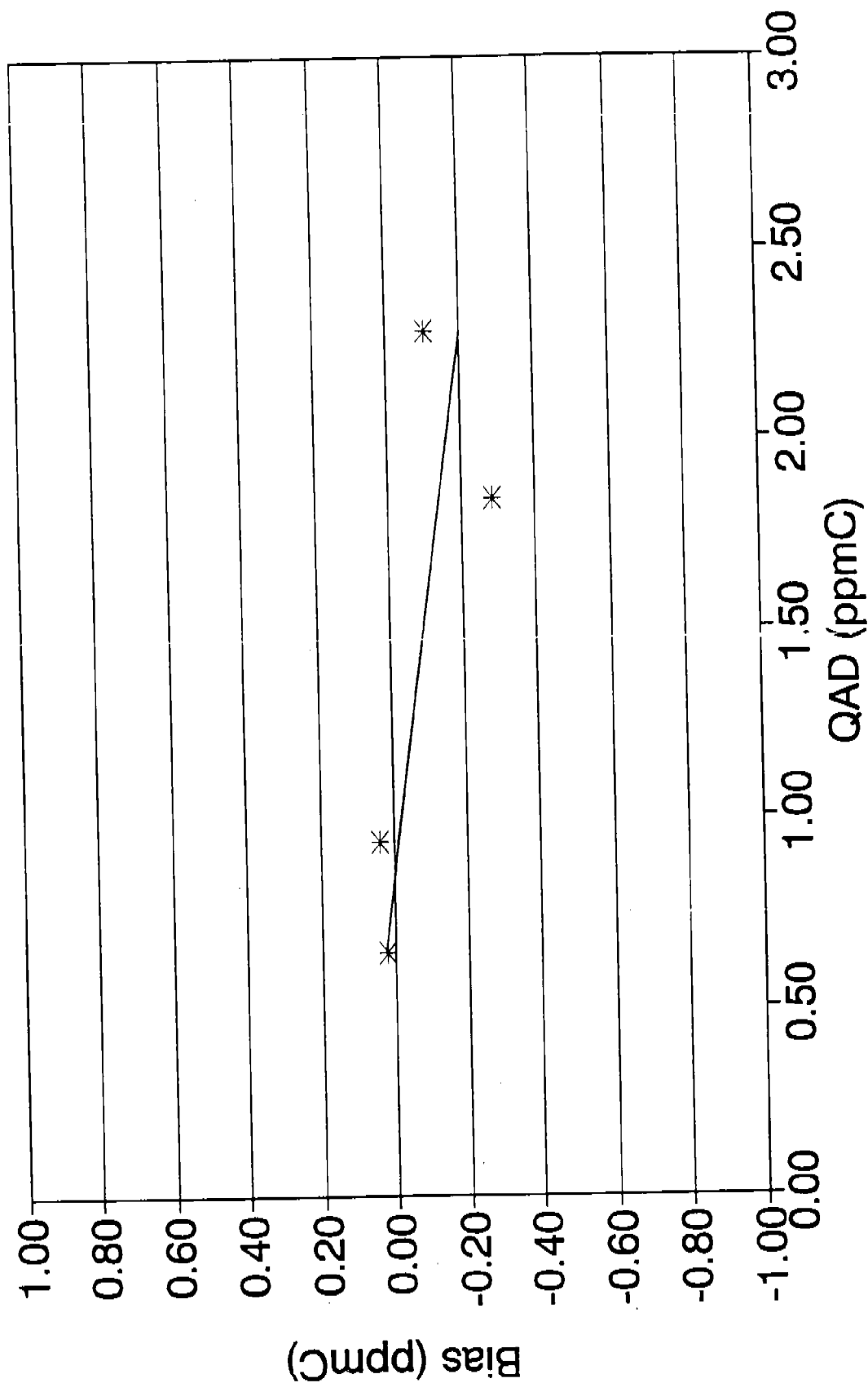


Figure 4-22. Audit bias, Radian Channel D vs. EPA-QAD.

TABLE 4-20. AUDIT SAMPLES, RELATIVE TO EPA-QUALITY ASSURANCE DIVISION (QAD) RESULTS

[illegible]

One hundred percent of the data base was validated according to the procedure outlined below.

A. Calibration factors were checked.

1. The area count from the strip chart that was used to determine the calibration factor was examined to verify that the data had been properly transferred to the calibration form.
2. The calibration form was examined to verify that the calculations had been correctly made.
3. Each datum on the disk was compared to the corresponding datum on the calibration sheet for accuracy.

B. Analysis data were checked.

1. Area counts were verified from the appropriate strip chart.
2. Calculations were reverified on the analysis forms.
3. Each datum on the disk was compared to the corresponding item on the analysis form.

C. Field data sheet was checked.

1. Each datum on the disk was compared to the corresponding datum on the field data sheet.

The error rate was calculated in terms of the number of items transferred from the original data sources. For each NMOC value in the 1990 data set, 36 items were transferred from original sources to the magnetic disks. In the data validation study each item on the disk was compared with the corresponding value on the original source of data. Two hundred and four errors were found (and corrected) for an expected error percentage of 0.956.

Each time the data file was opened and a suspected error found, the error was checked against the original archived documents, and corrected where appropriate.

4.10 NMOC MONITORING PROGRAM RECORDS

The quality assurance records developed by Radian for this project are extensive and will be preserved as archives. One of the most important objectives of the study was to develop a data base that is well planned and documented and contains NMOC data of known and verifiable quality. Achieving

that objective has involved keeping and preserving a number of records that trace the project from planning through reporting.

4.10.1 Archives

In order to keep detailed records that document the quality of the measurements made, Radian developed the following original material:

- Quality Assurance Project Plan (QAPP);
- Notebooks;
- Field Data Sheets;
- Laboratory Calibration Sheets;
- Laboratory Analysis Sheets;
- Chromatographic Strip Charts;
- EPA-QAD NMOC Results;
- Bi-weekly, Monthly Reports to EPA;
- Memoranda and Correspondence; and
- Final Report.

In addition to the above items, several papers to be presented at technical meetings and symposia and published in technical journals will be added to the archives.

The QAPP² was the Quality Assurance Project Plan and the workplan. The QAPP was designed according to the EPA Quality Assurance Guidelines, and set the pattern of steps necessary to document and control the quality of the data obtained throughout the study.

Several notebooks were necessary to maintain day-to-day records of the project. Field and laboratory data sheets were designed in advance, so that the data recorded appeared in a logical sequence and filled in blanks on the sheet. Additional space was provided for other comments. Each NMOC analysis was assigned a unique Radian Identification Number. Field data sheets and shipping records accompanied the canisters in transit.

4.10.2 Magnetic Disks

In order to manage the data base for report generation and data analysis, pertinent data from the various data sheets and notebooks were transferred to 20 megabyte magnetic disks. The following software was used in the construction of the data base: Paradox 3®, Lotus 1-2-3®, and PC File+®.

Statistical calculations were performed using SYSTAT® software. The data access is rapid and in a convenient form. The primary 20 megabyte magnetic disk has three backup disks.

5.0 NMOC DATA ANALYSIS AND CHARACTERIZATION

The purpose of this section is to characterize the NMOC data qualitatively as well as quantitatively. The NMOC data are shown to fit a two-parameter lognormal distribution better than a normal Gaussian distribution. The summary NMOC data for the sites of the 1990 study are given in Appendix E.

5.1 OVERALL CHARACTERIZATION

Figure 5-1 gives a stem-and-leaf plot of the 1990 Morning Site NMOC data along with statistics for NMOC. The stem-and-leaf plots show the actual NMOC concentrations truncated to two or three decimal points. The digits to the left of the vertical open space are called stems and the digits to the right of the open space are the leaves. The data are sorted from the smallest at the top of the graph to the largest at the bottom of the graph. The minimum NMOC value measured was 0.012 ppmC and is shown as "0 1" on the first row at the top of the plot. The maximum NMOC concentration measured was 14.254, shown as "142 50" in the bottom row of the chart. The plot shows 536 leaves, one for each NMOC Site datum in the 1990 program. The H's in the open vertical space locate the stem and leaf for the upper and lower hinges, and the M locates the stem and leaf for the median. The median separates the sorted NMOC concentrations into two equal halves; the hinges (or quartiles) separate each half into quarters. The "H spread" or inter-quartile range is the difference between the NMOC values of the two hinges.

Statistics shown for NMOC are number of cases, minimum, maximum, mean, median, standard deviation, standard error, skewness, kurtosis, and the two hinges. Each NMOC determination is the average of two or three injections of the site samples. Where duplicates were collected, the NMOC determination is the average of the two canister content concentrations. In the case of replicates, each NMOC determination is the average of the original and repeated analysis concentrations.

The standard error is the standard deviation divided by the square root of the number of cases. Positive skewness is a third moment about the mean value, and characterizes a tail to the right of the mean value. A normal Gaussian distribution has a skewness of zero. The skewness of 6.840 for the

```

0      1
0      55566 66788 89
1      00000 00111 11112 22223 33333 34444 444
1      55555 55555 56666 66666 67777 77777 78888 88888 89999 99999 9999
2      H 00000 01111 11122 22222 23333 33344 44444 44
2      55555 55666 67777 77778 88888 88888 89999 9999
3      00000 00111 11111 11111 22223 33333 33444 4
3      55555 66666 66677 77788 88888 88888 9999
4      M 00000 01111 11111 22223 33334 4444
4      55556 66667 77777 78888 88999 99
5      00000 01111 2244
5      55555 66667 7889
6      01111 12223 33344
6      55556 66666 77789 9
7      00122 23334 44
7      55555 66778 9
8      00123 33333 34
8      H 55667 78999
9      00012 2334
9      56788 899
10     0334
10     67888 8
11     12444
11     55666 77889 9
12     01233
12     6
13     12222 24
13     67899 9
14     11122 34
14     558
15     12222 3444
15
16     1
16     9
17     01133 3
17     78
18     1
18     46
19     338
20     34447 9
21     00689
22     9
23     337
25     8
27     7
28     9
30     9
31     2
32     16
33     2
34     236
38     3
40     04
41     2
42     8
62     0
142    5

```

NMOC, ppmC	
Cases	534
Minimum	0.012
Maximum	14.255
Mean	0.728
Standard Deviation	0.941
Standard Error	0.041
Skewness	6.830
Kurtosis	82.131
Lower Hinge(H)	0.245
Median(M)	0.439
Upper Hinge(H)	0.883

Figure 5-1. Stem-and-leaf plot of the 1990 NMOC data.

1990 NMOC data suggests a lognormal frequency distribution; that is supported by the fact that for the logarithm of the NMOC value ($\ln(\text{NMOC})$) (see Figure 5-2), skewness equals 0.16, which is close to zero. Kurtosis is the fourth moment about the mean and relates to the pointedness of the distribution. A distribution more pointed than a normal distribution, having the same standard deviation, has a kurtosis greater than 3.0.

Figure 5-2 is a stem-and-leaf plot of the 1990 $\ln(\text{NMOC})$ data. The plot shows an approximately symmetrical distribution (skewness = 0.16). The kurtosis equal to 0.204 indicates the $\ln(\text{NMOC})$ distribution to be less pointed than a normal distribution.

The shape of the stem-and-leaf plots suggests a lognormal distribution. Figures 5-3 and 5-4 support the lognormal distribution hypothesis for NMOC. The vertical scales in Figures 5-3 and 5-4 are arranged so that if the cumulative frequency of occurrence of NMOC were normally distributed, the numbers would plot into a straight line. The line in Figure 5-3 has a noticeable concave downward trend, indicating that the data do not fit a normal distribution well. Figure 5-4 plots the logarithm of NMOC on the same vertical scale. The fact that the digits on the graph plot into approximately a straight line supports the hypothesis that the NMOC data are approximately lognormally distributed. An asterisk on the graph indicates the location of a single datum. Integers, such as 2, 6, or 9, show the location of the corresponding number of data points. The number 999 shows the approximate location of either 27 data points or $99 + 9$ data points. The results, although qualitative, show a dramatic difference between the normal and lognormal hypotheses, and suggest that the latter more nearly describes the NMOC data. Figure 5-4 is labeled a "Normal Probability Plot," but since the independent variable is the logarithm (to the base e) of NMOC, if the relation between the EXPECTED VALUE and $\ln(\text{NMOC})$ is linear, a lognormal distribution is indicated.

5.2 MONTHLY VARIATIONS, 1984 - 1990

Table 5-1 partitions the NMOC data for the summer of 1990 into groups which correspond to monthly intervals.

```

-2 988
-2 77766
2 444
-2 33222 2222
-2 11111 10000 00000 000
-1 99999 99888 88888 88888 88888 8
-1 77777 77777 77666 66666 66666 66666 6
-1 H 55555 55555 55554 44444 44444 44444 44444
-1 33333 33333 33333 22222 22222 22222 22222 2
-1 11111 11111 11111 11111 11111 10000 00000 00000 000
-0 M 99999 99999 99999 99999 99999 88888 88888 88888 88888 88888
-0 77777 77777 77777 77777 77777 76666 66666 66666
-0 55555 55555 55555 44444 44444 44444 44444 44444
-0 33333 33333 33333 22222 22222 22222 22
-0 H 11111 11111 11111 11111 10000 00000 00000 00
0 00000 00000 11111 11111 11111 11111 1111
0 22222 22222 33333 33333 33333 3
0 44444 44444 55555 55555
0 66666 77777 77777 7
0 88889
1 00111 1
1 22223 33
1 44
1 8
2 6

```

In(NMOC)	
Cases	534
Minimum	-4.443
Maximum	2.657
Mean	-0.751
Standard Deviation	0.908
Standard Error	0.039
Skewness	0.161
Kurtosis	0.211
Lower Hinge(H)	-1.409
Median(M)	-0.823
Upper Hinge(H)	-0.124

Figure 5-2. Stem-and-leaf plot of the In(NMOC) data.

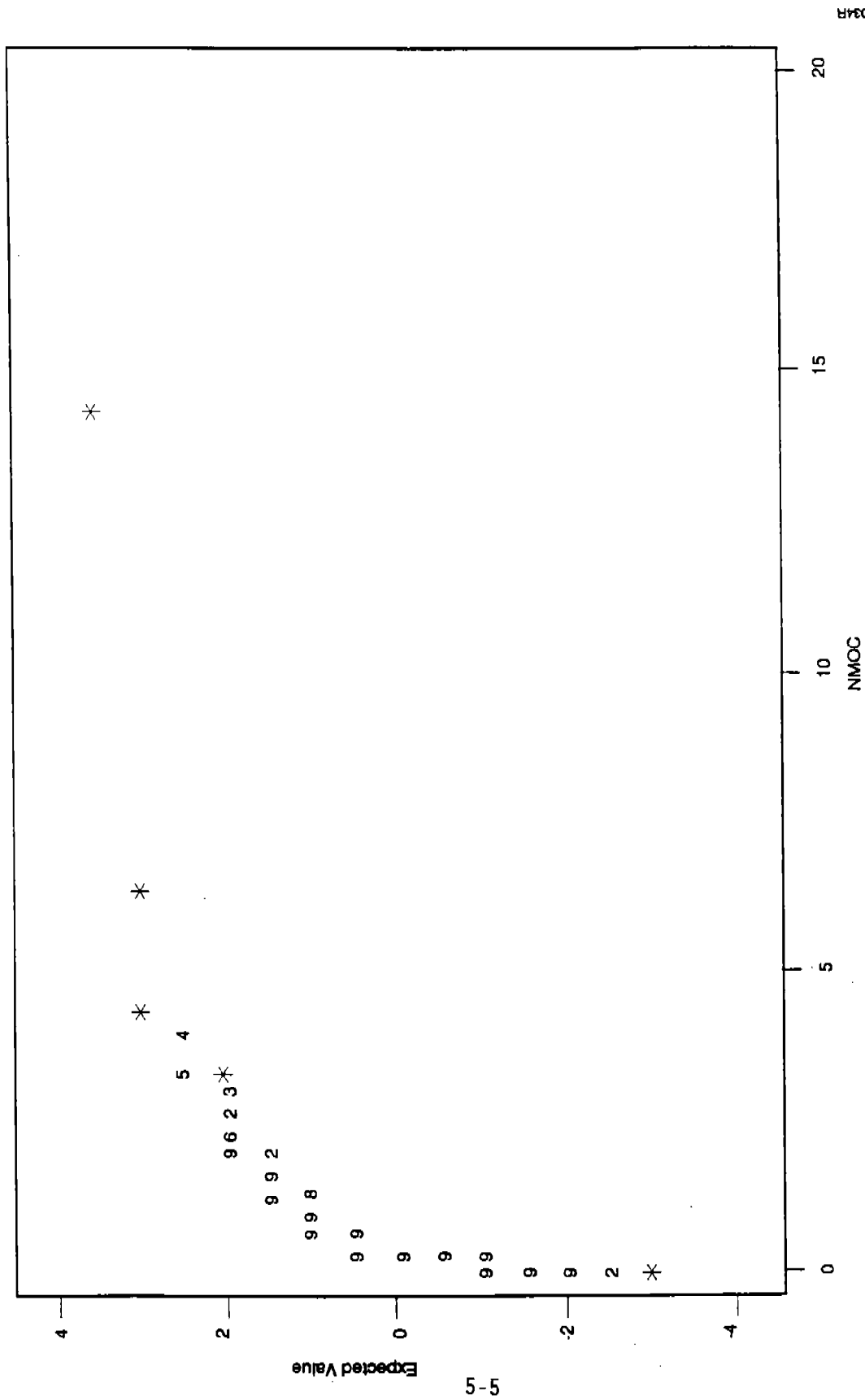


Figure 5-3. Cumulative frequency distribution for the 1990 NMOC data.

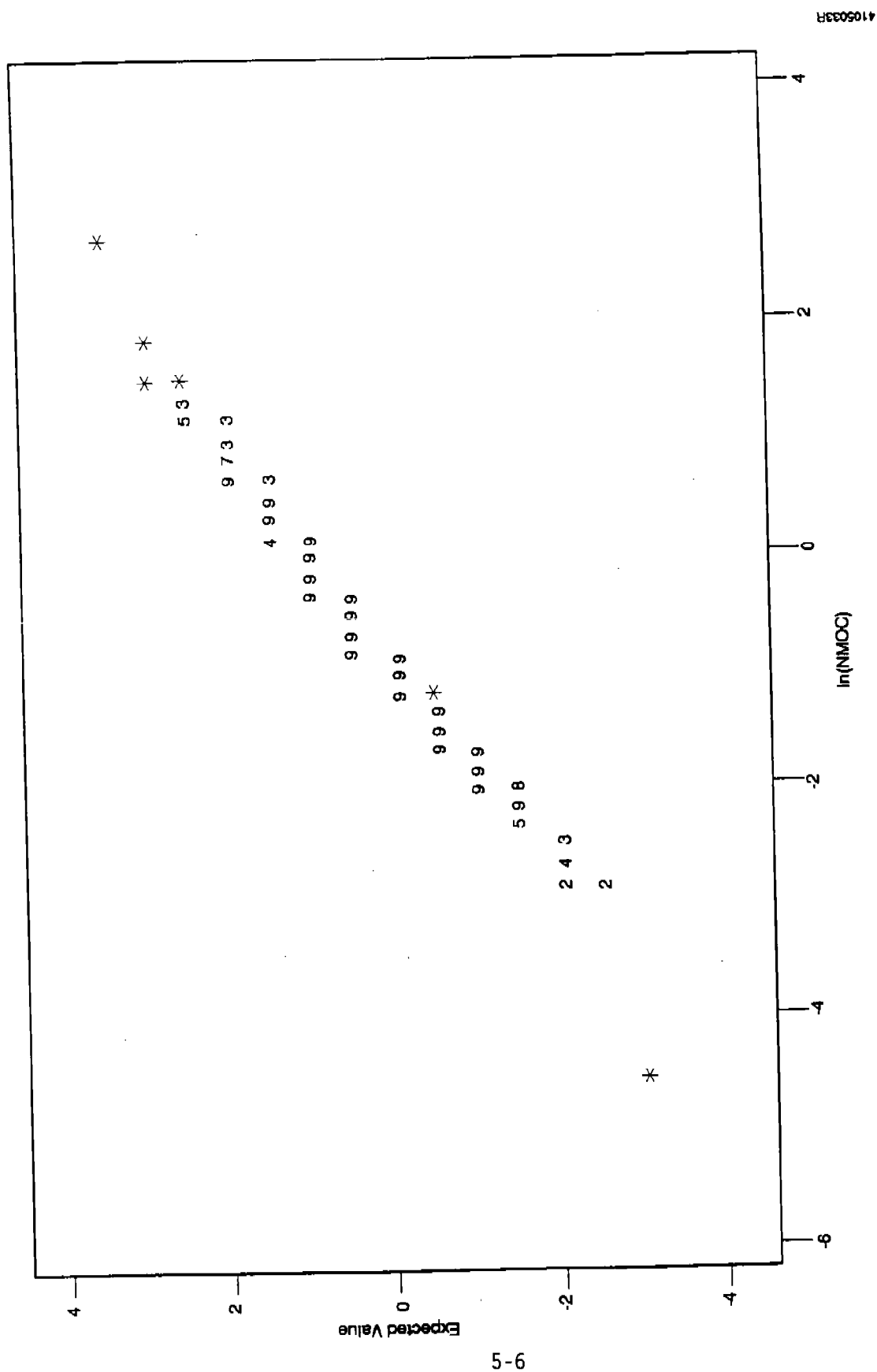


Figure 5-4. Cumulative frequency distribution for 1990 ln(NMOC) data.

TABLE 5-1. SUMMARY STATISTICS FOR 1990 NMOC SITES, BY MONTH

Sample Month 1990	Minimum NMOC ppmC	Median NMOC ppmC	Mean	Maximum	Standard Deviation	Cases
June	0.069	0.444	0.592	6.200	0.646	118
July	0.089	0.365	0.562	3.099	0.533	143
August	0.012	0.439	0.745	14.254	1.257	149
September	0.057	0.659	1.016	4.283	1.031	126

For the summer of 1990, the monthly means and medians of the NMOC sites for June, July, August, and September parallel one another. That is, the NMOC concentrations mean and median for July 1990 are less than the mean and median for June 1990. Means and median for August and September show dramatic increases compared to July 1990. Figure 5-9, in which monthly means for NMOC emissions are plotted for the years 1985 through 1990, the results show that September means are higher than August means for each year. This observation is particularly interesting because the number and location of the NMOC sites changes from year to year, and the average concentrations shown in Figure 5-9 are for all of the sites for a particular year. Arithmetic means are used in Table 5-1 in spite of the observations given in Section 5.1 which conclude that the frequency distribution of NMOC concentrations in ambient air are logarithmic normal distributed. Comparison of Tables 2-2 and 2-3 containing site average concentrations for the Gaussian and lognormal distributions, respectively, emphasize that the lognormal means may be less than, equal to, or greater than the respective arithmetic means. In all cases the means are within 10% of one another. Either the arithmetic means, or the mean of the lognormal distribution may be used as a measure of central tendency of the data. Table 5-1 also gives monthly minima, medians, and maxima. These latter three statistics are independent of the probability distribution from which they derive.

Figures 5-5 through 5-8 give the stem-and-leaf plots of the NMOC data for June, July, August, and September 1990, respectively. All the plots show the general shape of lognormal distribution. The data for June, July, August, and September may be considered typical of the sites tested during the indicated time period. Monthly mean NMOC emissions are plotted in Figure 5-9 for 1985, 1986, 1987, 1988, 1989 and 1990. No general trends are evident for the years shown. For all six years, September means are higher than August means, and for five of the six years, July means are less than June means. At present, however, it must be concluded that random behavior is responsible for apparent month-to-month changes.

During the seven years of the NMOC Monitoring Program, one site participated in the program for all seven years. Two sites have been in the


```

0      59
1      00112 35555 66889 999
2 H    00012 23455 57889 99
3      00112 33456 78888 8
4 M    00011 44557 77889 9
5      12456
6      11233 34556 6
7 H    34558 9
8      13356 789
9      0279
10     038
11     1568
12     01
13     9
15     2
17     11
20     7
62     0

```

NMOC, ppmC	
Cases	118
Minimum	0.069
Maximum	6.200
Mean	0.592
Standard Deviation	0.646
Standard Error	0.059
Skewness	5.820
Kurtosis	46.482
Lower Hinge(H)	0.256
Median(M)	0.444
Upper Hinge(H)	0.756

Figure 5-5. Stem-and-leaf plot of the NMOC data for June, 1990.

```

0      8
1      00011 11245 55666 67777 78888 99
2 H    00112 23333 44444 45556 77888 999
3 M    01111 11233 34556 66778 8899
4      11122 23344 66777 89
5      00112 668
6 H    069
7      01234 5
8      39
9      06
10     368
11     66
12     26
13     12
14     4
15     1128
16     12
17     1
18     37
19     33
20     9
21     0
22     3
23     9
30

```

NMOC, ppmC	
Cases	143
Minimum	0.089
Maximum	3.099
Mean	0.565
Standard Deviation	0.534
Standard Error	0.045
Skewness	1.982
Kurtosis	4.087
Lower Hinge(H)	0.231
Median(M)	0.365
Upper Hinge(H)	0.677

Figure 5-6. Stem-and-leaf plot of the NMOC data for July, 1990.

4105020R

```

0      15566 6788
1      00223 33444 45555 66788 99
2 H    01122 33456 66777 8888
3      00001 11234 55666 889
4 M    00011 33456 8899
5      01457 89
6      11223 45678 9
7      026
8 H    03334 6789
9      058
10     47
11     24577 8
12     3
13     22679 9
14     1245
15     234
16
17     038
18     4
19     8
20     344
23     3
25     8
31     2
142    5

```

NMOC, ppmC	
Cases	148
Minimum	0.012
Maximum	14.255
Mean	0.750
Standard Deviation	1.260
Standard Error	0.104
Skewness	8.508
Kurtosis	87.647
Lower Hinge(H)	0.239
Median(M)	0.442
Upper Hinge(H)	0.904

Figure 5-7. Stem-and-leaf plot of the NMOC data for August, 1990.

4105019R

```

0      01111 11111 11111 11111 1
0 H    22222 22222 23333 33333 333
0      44444 44445 55555 55
0 M    66666 67777 7777
0      88889 99999 99
1      00111 1
1 H    2333
1      44555
1      67
1      88
2      01111
2      23
2
2      7
2      8
3      22344 48
4      0012

```

NMOC, ppmC	
Cases	126
Minimum	0.057
Maximum	4.283
Mean	1.018
Standard Deviation	1.034
Standard Error	0.093
Skewness	1.608
Kurtosis	1.757
Lower Hinge(H)	0.298
Median(M)	0.658
Upper Hinge(H)	1.325

4105018R

Figure 5-8. Stem-and-leaf plot of the NMOC data for September, 1990.

NMOC MONITORING PROGRAM

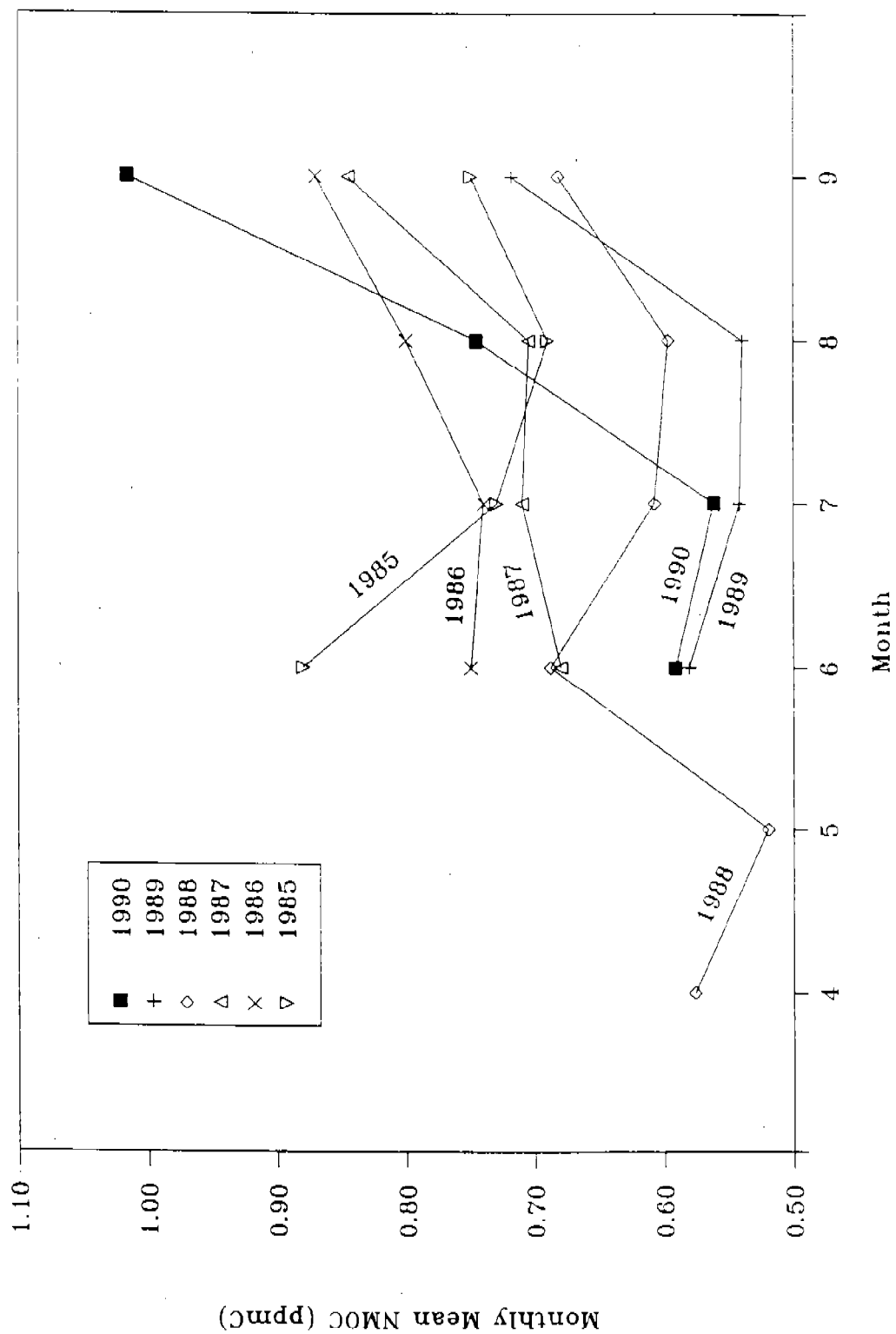


Figure 5-9. Monthly Mean NMOC Concentrations for 1985 Through 1990.

program 6 years; 4 sites for 5 years; 1 site for 4 years; 3 sites for 3 years; 12 sites for 2 years; and 73 sites for only 1 year. In all cases the sites were urban sites, but it is difficult to draw conclusions from year to year because of the difference in yearly site participation.

The April and May NMOC monitoring data for 1988 were from only four Florida sites, MIFL, M2FL, T1FL, and T2FL. The remainder of the points located on the 1988 trend line included data from 45 NMOC Monitoring Program sites.

6.0 RECOMMENDATIONS, NMOC MONITORING PROGRAM

Based on the experiences and results of past NMOC Monitoring Studies, certain recommendations can be made with respect to equipment design and validation procedures.

6.1 SITING CRITERIA

At urban centers experiencing extreme or severe ozone problems, additional NMOC monitoring sites should be located at strategic points in the urban center. A representative number of sites per urban center should be no less than four. At these sites, meteorological data, ozone data, and NO_x data should also be gathered.

6.2 OPERATING PROCEDURE CHANGES

Current operating procedures call for the use of dry propane standards and external audit samples, yet all the ambient air samples have water vapor in them. The effect of humidity on propane calibration (and audit) results is currently unknown and should be determined. The experimental design recommended to study this conundrum would cover the present NMOC span of 0 to 9 ppmC, and at least 3 levels of humidity: zero, low (-10%), and medium (-30%) relative humidity.

6.3 VERTICAL STRATIFICATION STUDY

In 1987, 1988, and 1989 ambient air samples were taken at ground level (3 to 10 meters) and at the 1197-foot (364.9 meter) level at one site. In 1988, an additional site was located on top of the World Trade Center in New York, a height of over 1000 ft. It is recommended that further study be performed at these sampling heights and that at least one more level (at 100 meters or some other appropriate height above ground level) be sampled at the same location. At the same time, barometric pressure and wind velocity and direction data should be obtained at each sampling level. These samples should be analyzed for NMOC content as well as for the air toxics compound concentrations. It is also recommended that ozone concentrations and NO_x concentrations be monitored at the same locations and altitudes. The information gained from such a study would be useful in validating various atmospheric model predictions.

6.4 SEASONAL NMOC STUDIES

Data derived in a study qualifying NMOC and NO_x in seasons other than summer could be useful in understanding the relationship of NMOC to NO_x and meteorological conditions. Currently a year-round study for 24-hour air toxics ambient air samples is being conducted. No study is currently in progress to determine seasonal NMOC concentration changes.

6.5 DIURNAL STUDIES

It is proposed that a diurnal study be made at an appropriate monitoring site to measure NMOC concentrations by the PDFID and CB-4 measurement techniques, 24-hours per day, seven days per week, for at least four weeks. An appropriate site for such a study would be one at which the NMOC concentration averaged 0.800 ppmC or greater, and one at which meteorological as well as NO_x data were available. Sampling plans could include both continuous NMOC measurement, and collection of integrated samples at various times through the day.

6.6 CANISTER CLEANUP STUDIES

The present canister cleanup procedure appears to be adequate for the NMOC program, since the concentrations of interest are at the ppmC level. However, the 3-Hour Air Toxics and UATMP, the concentration levels are at the ppbv levels, i.e., 0.01 to 50 ppbv, and the present canister cleanup procedure may not be sufficient to prevent significant carryover of target compounds from one sample to the next.

Additional cleanup studies are proposed to determine more specifically the carryover of organic material after cleaning, and to determine how storage of cleaned, evacuated canisters affects NMOC concentration of a sample. Storage effects up to three months under vacuum and under pressure should be included in the study.

Additional studies are proposed to compare cleanup procedures at room temperature with cleanup procedures involving heating of the canisters.

Radian has proposed⁷ initiation of several studies to determine whether the present canister cleanup procedure is adequate to prevent significant carryover of organic compounds from one canister to the next. These studies are needed since equilibration in a canister may take a week or longer.

The effect of sample pressure on the measured NMOC concentration is not clear. Ambient air samples are sufficiently humid so that at 15 psig, liquid water condenses inside the canister. Migration of liquid water to the canister walls affects the adsorption equilibrium, and at the same time, provides a medium for further depletion of the vapor phase organic compounds because of the solubility of organics in water. Equilibration under these conditions would take longer, perhaps 30 days or more, and the effect on the measured air sample NMOC (and UATMP target compound) concentration has not been determined. These effects, however, are probably not significant for the NMOC measurements, but could affect 3-hour air toxics measurements.

6.7 COORDINATED SAMPLING AT NMOC SITES

It is recommended that where possible the following sampling take place at NMOC sites for the 1991 monitoring programs:

- NMOC samples;
- CB-4 samples;
- Carbonyl samples;
- 3-hour air toxics compounds; and
- UATMP sampling (at least 38 target compounds).

This kind of program would effect some economy in setting up and monitoring the sampling program, and also provide some opportunity for cross-correlation of the results. It is recommended that meteorological data, temperature, barometric pressure, NO_x concentration, and possibly radiation intensity are continuously monitored at the sites.

Coordinated sampling would be most meaningful at sites where NMOC, CB-4, and/or UATMP monitoring occurred the previous year (or years).

6.8 FIELD AUDIT

It is recommended that a field audit be designed and conducted at several NMOC sites during the 1991 Monitoring Program. It is suggested that one field audit per month be performed at an NMOC site during June, July, August, and September 1991. The field audit should use at least one standard of known NMOC concentration and should collect duplicate samples plus a zero-air blank for each site. The audit samples should use both dry and humid standards.

6.9 DUPLICATE SAMPLE AND REPLICATE ANALYSIS

During the 1991 NMOC Monitoring Program records should be kept of (1) the NMOC concentration in a duplicate canister before cleanup, and (2) the zero-air NMOC concentration at the time of the third pressurization with clean, humidified zero air. The duplicate samples should be scheduled so that the same amount of time elapses between sampling and analysis for all duplicate samples.

7.0 THREE-HOUR AIR TOXICS DATA SUMMARY

The 1990 NMOC Program included three-hour air toxics samples at three NMOC urban sites (See Table 7-1) located in the contiguous United States. Overall concentration results are reported in parts per billion by volume (ppbv) in Section 7.1, and site-specific results are given in Section 7.2.

Analyses were done by a GC/MD system using flame ionization detection (FID), photoionization detection (PID), and electron capture detection (ECD). Compound identification was made using a combination of retention time, ratios of PID/FID and/or ECD/FID responses, and analyst experience and judgment. Quantitation was done using the FID response, with the exception of halogenated compounds that were quantitated using the ECD. If there was an indication that the quantitation detector response for the target compound had interference from an unknown source quantitation was performed on one of the alternate detectors if applicable. Table 7-1 indicates the number of 3-hour samples taken for GC/MD analyses to speciate for 38 UATMP compounds. About 10 analyses were performed on samples from each site. One duplicate sample was collected from each site, and the analysis of one of the samples from each site was replicated. One of the samples from each site was analyzed by gas chromatography/mass spectrometry (GC/MS) for confirmation of compound identification.

Three-hour air toxics samples were regular NMOC Monitoring Program samples that were collected in 6-L stainless steel canisters from 6:00 a.m. to 9:00 a.m. The final canister pressure was about 15 psig. The NMOC samples that were speciated by GC/MD were selected at random during the summer. Each selected sample was first analyzed by the PDFID method for its NMOC concentration. Then the canister pressure was bled to atmospheric pressure and the canister bellows valve was closed. The canister was allowed to equilibrate at least 18 hours before the GC/MD analysis was performed.

7.1 OVERALL RESULTS

Concentrations of the air toxic compounds detected are summarized in Table 7-2 for the 1990 3-hour ambient air samples that were speciated. The table shows the number of cases (samples), the percent of cases in which the

TABLE 7-1. THREE-HOUR AMBIENT AIR SAMPLES AND ANALYSES

Site Code	No.	Duplicate Pairs	GC/MD Analyses		GC/MS Analyses
			Replicate	Total	
BRLA	9	1	1	11	1
NWNJ	8	1	1	10	1
PLNJ	<u>8</u>	<u>1</u>	<u>1</u>	<u>10</u>	<u>1</u>
Total	25	3	3	31	3

TABLE 7-2. COMPOUND IDENTIFICATION WITH GC/MD FOR ALL 3-HOUR SITES

Compounds	Cases		Minimum ppbv	Maximum ppbv	Mean ppbv
	%	No.			
1,3-Butadiene	58	18	0.11	6.83	1.98
Chloromethane	3	1	0.06	0.06	0.06
Chloroethane	6	2	0.08	0.31	0.20
Methylene chloride	6	2	0.92	2.69	1.80
trans-1,2-Dichloroethylene	10	3	0.31	0.72	0.48
Chloroprene	68	21	0.03	1.78	0.46
Chloroform	13	4	0.16	0.72	0.39
1,1,1-Trichloroethane	100	31	0.19	12.32	1.15
Carbon tetrachloride	100	31	0.05	0.30	0.15
Benzene	100	31	0.27	5.92	1.65
Trichloroethylene	29	9	0.09	0.97	0.39
1,2-Dichloropropane	48	15	0.07	1.51	0.74
Bromodichloromethane	3	1	0.12	0.12	0.12
Toluene	100	31	0.78	13.34	4.08
n-Octane	19	6	0.004	0.46	0.26
1,1,2-Trichloroethane	16	5	0.14	5.06	3.41
Tetrachloroethylene	90	28	0.05	3.73	0.72
Chlorobenzene	13	4	0.01	0.08	0.06
Ethylbenzene	100	31	0.06	1.07	0.40
m/p-Xylene	100	31	0.32	6.24	1.94
Styrene/o-Xylene	100	31	0.16	2.72	1.02
m-Dichlorobenzene	16	5	0.02	0.05	0.03
p-Dichlorobenzene	16	5	0.30	1.68	0.90
o-Dichlorobenzene	6	2	0.22	9.27	4.74
Propylene	100	31	0.58	20.60	5.64
trans-1,3-Dichloropropylene	6	2	0.73	2.69	1.71

compound was identified, the minimum, maximum, and mean (arithmetic average) concentrations of the compound in ppbv. In cases where duplicate samples were taken, or replicate analyses were performed, the results of all the analyses were averages for each sample. The mean refers to the daily sample averages, not the averages of all the analyses. The target compounds identified fall into at least four categories: (1) those occurring in more than 70% of the samples tested, (2) those occurring in from 40% to 69% of the samples, (3) those occurring in less than 30% of the samples, and (4) those not identified in any of the 3-hour air samples at concentrations above their method detection limits. These results are summarized in Table 7-3.

Overall concentrations ranged from 0.004 ppbv for n-octane to 20.60 ppbv for propylene.

7.2 SITE RESULTS

Table 7-4 gives 3-hour ambient air concentrations by site code for the 38 target air toxics compounds. The overall site means range from 1.12 ppbv for PLNJ to 2.34 for BRLA. Appendix H tabulates the complete analytical results and includes the NMOC concentrations for each of the 3-hour air toxics samples.

TABLE 7-3. FREQUENCY OF OCCURRENCE OF TARGET COMPOUNDS
IN 3-HOUR AMBIENT AIR SAMPLES

Range for Frequency of Occurrence	Target Compounds	
100% to 70%	1,1,1-Trichloroethane Benzene Tetrachloroethylene m/p-Xylene Propylene	Carbon tetrachloride Toluene Ethylbenzene Styrene/o-Xylene
69% to 40%	1,3-Butadiene 1,2-Dichloropropane	Chloroprene
39% to >0%	Chloromethane Methylene chloride Chloroform Bromodichloromethane 1,1,2-Trichloroethane m-Dichlorobenzene o-Dichlorobenzene	Chloroethane trans-1,2-Dichloroethylene Trichloroethylene n-Octane Chlorobenzene p-Dichlorobenzene trans-1,3-Dichloropropylene
Zero	Acetylene Bromomethane Bromochloromethane cis-1,3-Dichloropropylene Bromoform	Vinyl chloride 1,1-Dichloroethane 1,2-Dichloroethane Dibromochloromethane 1,1,2,2-Tetrachloroethane

TABLE 7-4. COMPOUND IDENTIFICATIONS WITH GC/MD BY SITE CODE

Site	Compound	Cases	Minimum ppbv	Maximum ppbv	Mean ppbv
BRLA	1,3-Butadiene	8	0.44	6.83	4.15
	trans-1,2-Dichloroethylene	3	0.31	0.72	0.48
	Chloroprene	7	0.26	1.78	0.87
	Chloroform	2	0.37	0.72	0.55
	1,1,1-Trichloroethane	11	0.29	0.52	0.41
	Carbon tetrachloride	11	0.14	0.30	0.19
	Benzene	11	1.00	5.90	2.86
	1,2-Dichloropropane	6	0.91	1.46	1.24
	Toluene	11	1.76	8.18	4.38
	n-Octane	2	0.34	0.46	0.40
	1,1,2-Trichloroethane	3	4.23	5.06	4.66
	Tetrachloroethylene	10	0.05	1.68	0.34
	Chlorobenzene	1	0.08	0.08	0.08
	Ethylbenzene	11	0.25	0.98	0.48
	m/p-Xylene	11	0.86	4.81	2.22
	Styrene/o-Xylene	11	0.57	2.61	1.22
	m-Dichlorobenzene	3	0.03	0.05	0.04
	p-Dichlorobenzene	3	0.30	1.52	0.77
	Propylene	11	2.63	20.60	10.90
	trans-1,3-Dichloropropylene	2	0.73	2.69	1.71
NWNJ	1,3-Butadiene	6	0.11	0.46	0.21
	Chloroethane	2	0.08	0.31	0.20
	Chloroprene	5	0.03	0.64	0.36
	Chloroform	1	0.31	0.31	0.31
	1,1,1-Trichloroethane	10	0.70	2.16	1.28
	Carbon tetrachloride	10	0.13	0.18	0.14
	Benzene	10	0.50	2.24	0.88
	Trichloroethylene	6	0.10	0.97	0.48
	1,2-Dichloropropane	5	0.10	1.51	0.53
	Bromodichloromethane	1	0.12	0.12	0.12
	Toluene	10	2.01	11.49	4.32
	n-Octane	2	0.33	0.34	0.34
	Tetrachloroethylene	10	0.14	3.73	0.85
	Chlorobenzene	1	0.07	0.07	0.07
	Ethylbenzene	10	0.19	1.07	0.41
	m/p-Xylene	10	0.81	6.24	2.10
	Styrene/o-Xylene	10	0.52	2.72	1.06
	p-Dichlorobenzene	2	0.50	1.68	1.09
	o-Dichlorobenzene	1	9.27	9.27	9.27
	Propylene	10	0.92	8.10	3.08

(Continued)

TABLE 7-4. (Continued)

Site	Compound	Cases	Minimum ppbv	Maximum ppbv	Mean ppbv
PLNJ	1,3-Butadiene	4	0.18	0.47	0.28
	Chloromethane	1	0.06	0.06	0.06
	Methylene chloride	2	0.92	2.69	1.81
	Chloroprene	9	0.06	0.35	0.19
	Chloroform	1	0.16	0.16	0.16
	1,1,1-Trichloroethane	10	0.19	12.32	1.82
	Carbon tetrachloride	10	0.05	0.15	0.13
	Benzene	10	0.27	3.00	1.09
	Trichloroethylene	3	0.09	0.34	0.22
	1,2-Dichloropropane	4	0.07	0.62	0.26
	Toluene	10	0.78	13.34	3.49
	n-Octane	2	0.00	0.07	0.04
	1,1,2-Trichloroethane	2	0.14	2.91	1.53
	Tetrachloroethylene	8	0.16	3.13	1.04
	Chlorobenzene	2	0.01	0.08	0.05
	Ethylbenzene	10	0.06	1.01	0.31
	m/p-Xylene	10	0.32	4.84	1.48
	Styrene/o-Xylene	10	0.16	2.40	0.77
	m-Dichlorobenzene	2	0.02	0.03	0.03
	o-Dichlorobenzene	1	0.22	0.22	0.22
	Propylene	10	0.58	8.96	2.40

8.0 THREE-HOUR AIR TOXICS TECHNICAL NOTES

This section describes the equipment used to sample and analyze the 3-hour air toxics samples. Also described are sample handling procedures, sampler certification procedures, standards generation and instrument calibration procedures, compound identification procedures, GC/MS compound identification confirmation, quality assurance/quality control procedures, and data records for the 3-hour air toxics compounds.

8.1 SAMPLING EQUIPMENT AND INTERFACE

The sampling equipment for the 3-hour air toxics samples was the NMOC Monitoring Program sampling equipment described in Section 3.1. The original sample was collected as an integrated ambient air sample from 6:00 a.m. to 9:00 a.m. with a final sample pressure of about 15 psig. As stated above, after NMOC analysis the canister was bled to atmospheric pressure and allowed to stand at least 18 hours before being analyzed by GC/MD.

An interface system was designed and built by Radian Corporation to take a sample from the canister and inject it into the gas chromatograph for analysis.

Figure 8-1 shows the GC/MD system including the Sample Interface System, Analytical System, and Data System. The sample interface takes a 250-mL sample approximately from the canister, draws it through Trap Assembly 1 and condenses all the water and organic compounds, with the exception of methane, in the air sample drawn from the canister. Trap Assembly 1 is a cryogenic, liquid argon trap packed with glass beads. The cryogen is removed, and an electrical heater quickly heats Trap Assembly 1, vaporizing the water and organic compounds condensed from the canister sample.

8.2 THREE-HOUR AIR TOXICS SAMPLING SYSTEMS CERTIFICATION

The sampling systems used to collect 3-hour air toxics samples were certified for use per the specifications described in U.S. EPA Compendium of Methods TO-14.¹²

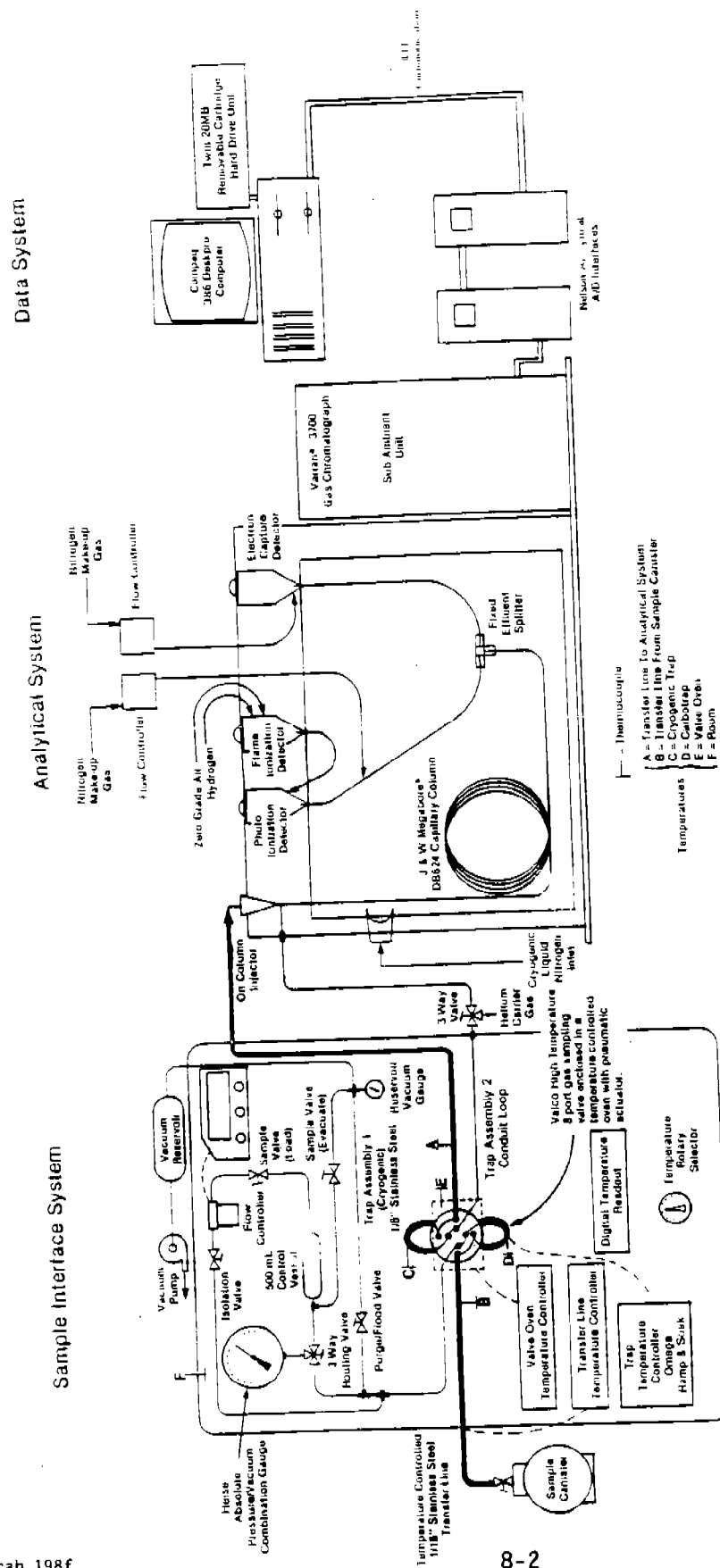


Figure 8-1. Gas chromatographic multidetector system.

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8.2.1 Sampler Certification Blanks - Humidified Zero Air

Zero certification consisted of purging the sampler with cleaned, humidified air, followed by collecting a sample of the cleaned, dried air that had been humidified through the purged NMOC samplers for GC/MD analysis. The purpose of the wet purge was to help remove any adherent contaminants from the sampler. The chromatograms from these certification sample analyses were archived for each sampler. Results presented in Table 8-1 showed a range of 0.002 ppmC to 0.005 ppmC of NMOC, with an average of 0.004 ppmC. The sampling systems were determined to be very clean and showed no characteristics of additive bias.

8.2.2 Sampler Certification Challenge - Selected Target Compound

Following the NMOC sampler blank certification, a challenge gas containing five selected target compounds was passed through the samplers. The average concentration of the compounds in the challenge gas was 18.5 ppbv/species. Table 8-2 shows the average system percent bias calculated with the analysis of the challenge gas being used as a reference concentration.

System percent bias ranged from 1.5% to 11.9% with an overall average of 8.2 percent. The systems showed acceptable subtractive bias characteristics.

8.3 STANDARDS GENERATION

The GC/MD analytical equipment was calibrated daily with a gas mixture that averaged 5 ppbv of each of the 38 target compounds at 70% relative humidity.

The standard gas mixtures were generated by dynamic flow dilutions of Scott certified gas mixtures with cleaned, dried air that had been humidified with HPLC-grade water. The Scott gas mixtures were dry and contained in cylinders under pressure at a concentration of 500 ppbv for all of the standards. The concentration for each target gas in the 500 ppbv Scott cylinder was certified to within ± 10 percent.

TABLE 8-1. SAMPLER CERTIFICATION ZERO RESULTS

Canister Number	Canister Blank Date	Blank Sample Concentration (ppmC)	Sampler System Number	Sampler Zero Collection Date	Sampler Zero Sample (ppmC)	Difference (ppmC)
052	6-05-90	0.003	22	6-06-90	0.005	-0.002
087	3-16-90	0.003	3	3-19-90	0.002	-0.001
101	3-16-90	0.001	6	3-19-90	<u>0.004</u>	0.003
				Average	0.004	

TABLE 8-2. SAMPLER CERTIFICATION CHALLENGE RESULTS

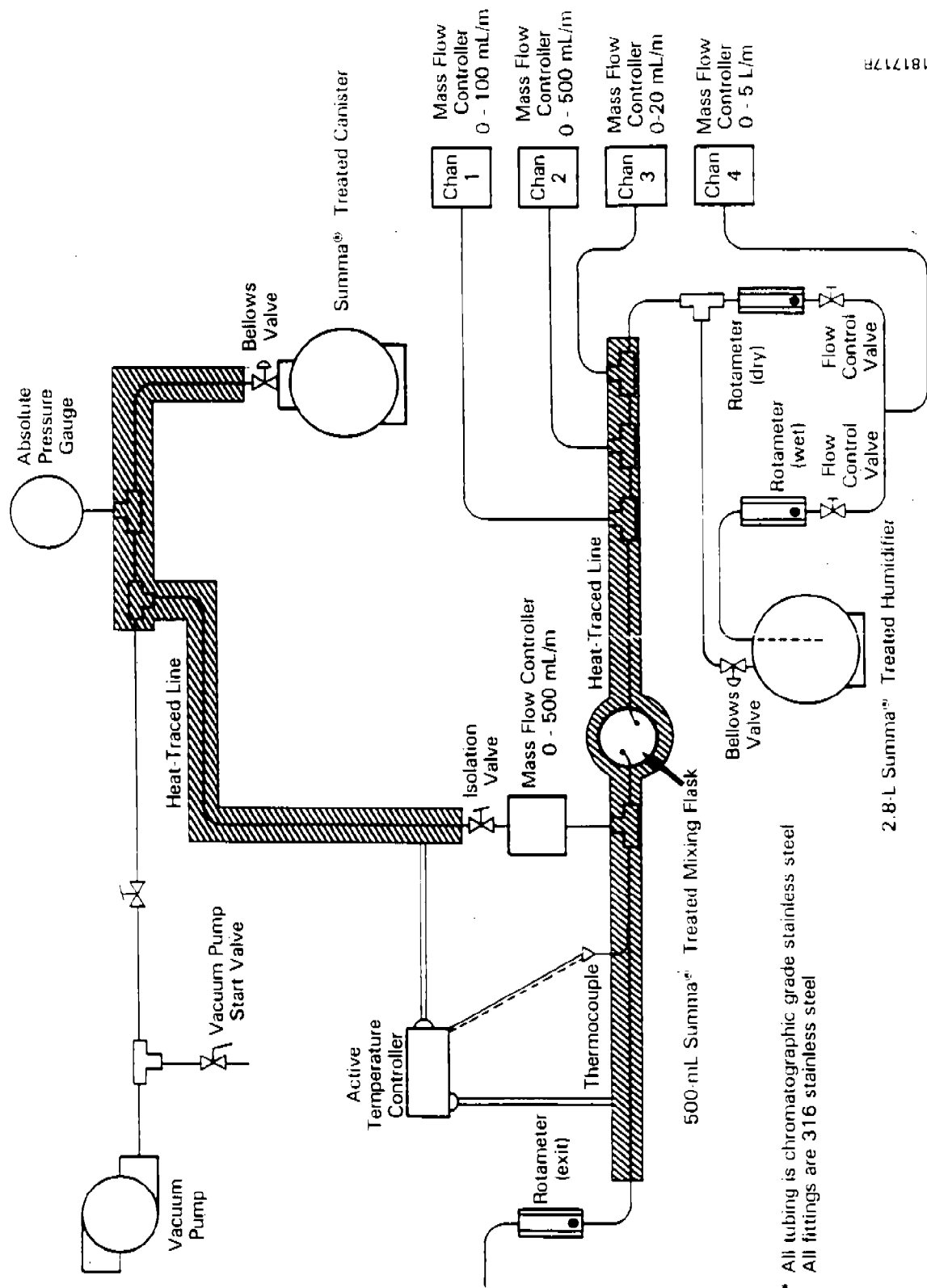
System Number	Percent	
	Average Compound Recovery	System Bias
22	101.5	1.5
3	111.9	11.9
6	<u>113.3</u>	<u>11.3</u>
Average	108.9	8.2

Figure 8-2 diagrams the dynamic flow dilution apparatus. One Scott cylinder contains 18 of the air toxics target compounds, a second Scott cylinder contains eight target compounds, a third Scott cylinder contains eleven target compounds, while the fourth cylinder contains only one target compound. The four Scott cylinders were connected to Channels 2, 3, 5, and 6 of the flow dilution apparatus. The fourth channel was connected to a cylinder of zero-grade air by way of a catalytic oxidizer that oxidized all of the hydrocarbon material in the zero-grade air. The five mass flow controllers were set to flow rates that would give the desired final concentration of the diluted gas.

The cleaned zero-grade air was partially humidified by bubbling part of the air stream through HPLC-grade water contained in a stainless steel canister. The wet and dry rotameters and all the mass flow controllers were calibrated with a bubble flowmeter before being connected to the flow dilution apparatus. All of the flow controllers, the connecting lines, and the mixing flask were heat traced to reduce adsorption of the target compounds. The temperature controller that regulated electrical current flow to the heat tracing was set for 100°C.

To generate a standard, the following procedure is used. The canister into which the standard is being mixed is connected to the flow dilution apparatus at the bellows valve shown in Figure 8-2. The temperature controller for the heat tracing is activated. The mass flow controllers are then set for the appropriate flow rate to obtain the desired dilution and the humidifier, lines, and mixing flask are purged for at least 10 minutes. The isolation valve is closed and the vacuum pump turned on. The tubing, the canister, and the absolute pressure gauge are all evacuated initially to about 0.5 mm Hg absolute pressure. The vacuum pump is then isolated from the system and the isolation valve is opened to the diluted gas mixture. The standard mixture fills the canister at a controlled rate until atmospheric pressure is reached. The canister with the diluted standard is disconnected from the flow dilution apparatus and allowed to equilibrate before use. The barometric pressure and room temperature are also recorded.

In order to calculate the exact concentration of each target compound in the standard mixture, a correction is made for the residual gas in the



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Figure 8-2. Dynamic flow dilution apparatus.

standard canister before the filling with the diluted gas is begun. A correction also is made for the water vapor added to the dilution air.

8.4 CALIBRATION ZERO AND SPAN

Most of the compound quantitation is performed with the calibrated response of the FID detector. For purposes of compound identification and quantitation (when there may be interference on the FID detector) it is also necessary to calibrate the PID and ECD responses. Initial calibration curves for each compound were generated on all three detectors with calibration standards at 1, 5, and 10 ppbv. In addition to the usual response (area counts) versus concentration curves, response times and response ratios for PID/FID and ECD/FID were determined for each target compound.

8.5 GAS CHROMATOGRAPH/MULTIDETECTOR ANALYSIS AND COMPOUND IDENTIFICATION

A Varian® 3700 gas chromatograph, configured with a PID in series with an FID and an ECD operating in parallel, performed the air toxics analyses. Fused silica was used for the detector-to-detector connections. The Air Toxics Multiple Detector System is shown in Figure 8-3 and diagrams the effluent splitter and multidetectors connected to the end of the Megabore® DB-624 capillary column.

The entire GC/MD system is shown in Figure 8-1, including the sample interface, the gas chromatograph/multidetector analytical system, and the data handling system. Sample volumes for the GC/MD analyses were about 250-ml.

Compound identification was performed using measured retention times and ratios of PID/FID and ECD/FID responses. The analyst's skill and experience was also needed in making a judgment about the presence or absence of a target compound because of the variability of retention times, and the presence of interfering compounds.

8.6 GAS CHROMATOGRAPH/MASS SPECTROMETER ANALYSIS AND COMPOUND IDENTIFICATION CONFIRMATION

Three of the 3-hour air toxics samples were analyzed by GC/MS for compound identification confirmation following completion of the GC/MD analyses. So that the sensitivity of the GC/MS compared favorably with that of the GC/MD, the GC/MS was operated in the multiple ion detection (MID) mode, and the sample volume was about 500-ml (compared to 250-ml for the GC/MD analyses).

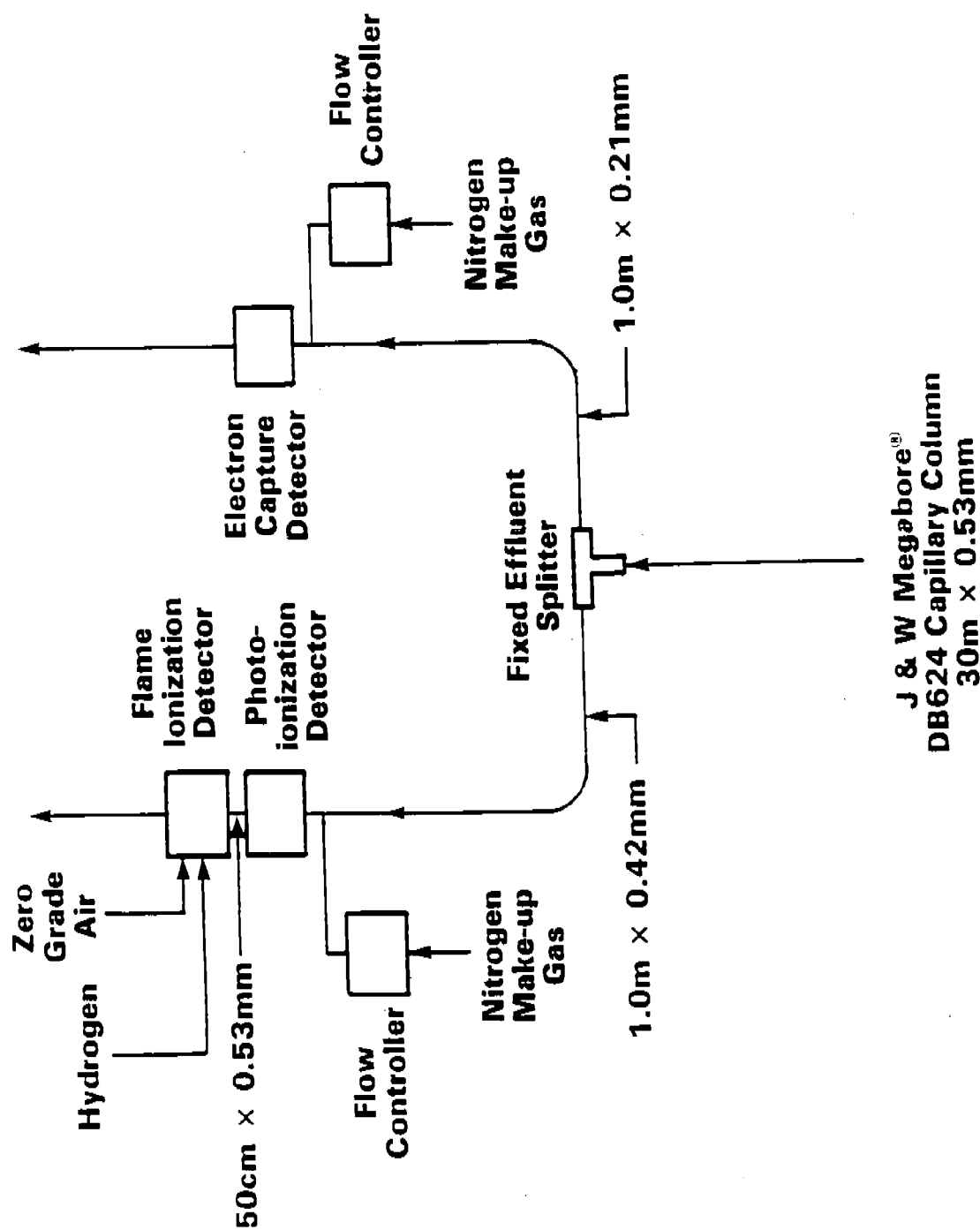


Figure 8-3. Air toxics multiple detector system.

No comparison of the quantitative results for GC/MS and GC/MD was made, because the purpose of the GC/MS analyses was compound identification confirmation only. This comparison is discussed below in Section 8.7.4.

8.7 QA/QC DATA

Quality assurance and quality control in the 3-hour air toxics data included a determination of method detection limits (MDL) for both the GC/MD and the GC/MS analytical methods.

One of the objectives of the UATMP was to make the MDLs as low as possible, recognizing that the lower MDLs may increase the number of false positive or false negative identifications. Other quality measures reported here involved analytical precision results from repeated analyses, and sampling and analysis precision from duplicate samples. Accuracy was assessed for both the GC/MD and GC/MS using external audits supplied by the EPA-QAD.

8.7.1 GC/MD and GC/MS Minimum Detection Limits

MDLs for the GC/MD and GC/MS analytical systems used in this study are given in Table 8-3. MDLs for the GC/MD analytical system are estimated from the minimum area count that reflects approximately three times noise for every compound and are based on a sample approximately 250-mL in volume. The sample volume for the GC/MS system was about 500-mL. The GC/MS was operated in the MID mode, which detected specific ions representative of the 38 air toxics target compounds.

8.7.2 Repeated Analyses

Repeated analyses were performed on three site samples by GC/MD. The analyses were performed on consecutive days with at least 24 hours between removing samples from the canister. From these analyses there were 31 cases in which a concentration for a target compound was found in both replicate analyses. Statistics for these data are summarized in Table 8-4, showing the overall minima, maxima, and means of the mean concentrations, standard deviations, coefficients of variation, and absolute percent differences for the replicate pairs. The absolute percent difference averages 26.430%, which is excellent agreement.

TABLE 8-3. METHOD DETECTION LIMITS FOR 3-HOUR AIR TOXICS COMPOUNDS

Compound	GC/MD MDL ppbv	GC/MS MDL ppbv
Acetylene	1.00	- ^a
Propylene	0.10	0.40
Chloromethane	0.20	0.56
Vinyl chloride	0.20	0.44
1,3-Butadiene	0.10	0.57
Bromomethane	0.20	0.25
Chloroethane	0.10	0.38
Methylene chloride	0.11	0.31
trans-1,2-Dichloroethylene	0.04	0.39
1,1-Dichloroethane	0.04	0.53
Chloroprene	0.06	0.57
Bromochloromethane	0.003	0.48
Chloroform	0.006	0.27
1,1,1-Trichloroethane	0.001	0.70
Carbon tetrachloride	0.001	0.37
1,2-Dichloroethane	0.04	0.59
Benzene	0.04	0.34
Trichloroethylene	0.004	0.37
1,2-Dichloropropane	0.04	0.44
Bromodichloromethane	0.001	0.22
trans-1,3-Dichloropropylene	0.04	0.50
Toluene	0.02	0.50
n-Octane	0.03	0.29
cis-1,3-Dichloropropylene	0.04	0.81
1,1,2-Trichloroethane	0.02	0.22
Tetrachloroethylene	0.07	0.32
Dibromochloromethane	0.001	0.25
Chlorobenzene	0.02	0.57
Ethylbenzene	0.02	0.72
m/p-Xylene	0.04	0.46
Styrene/o-Xylene	0.02	-
Styrene	-	0.46
o-Xylene	-	0.39
Bromoform	0.001	0.27
1,1,2,2-Tetrachloroethane	0.002	0.37
m-Dichlorobenzene	0.02	0.28
p-Dichlorobenzene	0.09	0.56
o-Dichlorobenzene	0.02	0.37

^aBelow mass spectrometry range.

TABLE 8-4. 3-HOUR AIR TOXICS REPLICATE ANALYSES BY GC/MD

Statistics	Minimum	Maximum	Overall Mean
Mean Concentration, ppbv	0.075	9.435	1.512
Standard Deviation, ppbv	0.000	0.587	0.072
Percent Coefficient of Variation	0.000	69.305	6.942
Absolute Percent Difference	0.000	100.000	26.430

Table 8-5 lists the cases in which a target compound was found in only one of the replicate analyses. Although the list of single compound identifications is not long, no pattern to the behavior emerges.

8.7.3 Duplicate Sample Results

Six duplicate 3-hour ambient air samples were analyzed by GC/MD for the 38 target compounds. Summary precision results are given in Table 8-6 in terms of mean concentration and concentration range in ppbv. Other precision statistics are given in terms of standard deviation, percent coefficients of variation, and absolute percent difference. The data in Table 8-6 are accumulated over all compounds and site locations.

The percent coefficients of variation ranged from 1.418% to 93.274%, averaging 15.272 percent.

Table 8-7 also shows that the imprecision is also compound specific. The compound absolute percent difference means ranged from 3.636 to 89.878 percent. The precision for the 3-hour air toxics compounds is good with an overall average absolute percent difference of 21.6 percent.

Table 8-8 lists the compounds that were identified in only one of the duplicate sample analyses. Again, no pattern to the behavior emerges.

8.7.4 GC/MS Confirmation Results

Based on three GC/MS analyses of the 3-hour air toxics samples, one from each site location, the following results were obtained. The GC/MS analyses confirmed 88.57% of the GC/MD analyses. The results are summarized in Table 8-9, showing 27.62% positive GC/MD-positive GC/MS confirmation, 1.90% positive GC/MD-negative GC/MS confirmation, 9.52% negative GC/MD-positive GC/MS comparisons, and 60.95% negative GC/MD-negative GC/MS comparisons.

8.7.5 External Audits

The external audit for the 3-hour air toxics compounds is conducted bimonthly on the Urban Air Toxics Program and the results will be reported in the 1990 UATMP Final Report. The audit samples that are used are furnished by the Quality Assurance Division of the U.S. EPA.

TABLE 8-5. SINGLE COMPOUND IDENTIFICATIONS OF GC/MD
REPLICATE SAMPLE ANALYSES

Compound	Concentration ppbv	Radiat ID
Chloroprene	0.51	1311 R1
Trichloroethylene	0.22	1293 R2
1,2-Dichloropropane	1.51	1285 R1
1,2-Dichloropropane	0.16	1293 R1
1,1,2-Trichloroethane	5.06	1310 R1
Chlorobenzene	0.08	1310 R2
p-Dichlorobenzene	1.52	1310 R2

TABLE 8-6. THREE-HOUR AIR TOXICS DUPLICATE SAMPLE ANALYSES BY GC/MD^a

Statistics	Minimun	Maximum	Overall Mean
Mean Concentration, ppbv	0.070	10.080	1.384
Standard Deviation, ppbv	0.003	1.633	0.186
Percent Coefficient of Variation	1.418	93.274	15.272
Absolute Percent Difference	2.005	131.910	38.399

^aBased on first analysis of contents of each duplicate canister.

TABLE 8-7. GC/MD 3-HOUR AIR TOXICS DUPLICATE PRECISION BY COMPOUND

Compound	Cases	Mean SD	Mean % CV	Mean Absolute % Diff
1,3-Butadiene	1	0.156	2.571	3.636
Chloroprene	2	0.166	29.258	41.377
1,1,1-Trichloroethane	3	0.124	11.114	15.717
Carbon tetrachloride	3	0.006	4.060	5.742
Benzene	3	0.148	12.372	17.496
Trichloroethylene	1	0.038	10.490	14.835
1,2-Dichloropropane	2	0.028	5.643	7.980
Toluene	3	0.316	11.018	15.582
Tetrachloroethylene	3	0.816	63.553	89.878
Ethylbenzene	3	0.038	11.472	16.225
m/p-Xylene	3	0.111	8.938	12.641
Styrene/o-Xylene	3	0.045	5.814	8.223
Propylene	3	0.255	12.034	17.019

TABLE 8-8. SINGLE COMPOUND IDENTIFICATIONS OF GC/MD DUPLICATE SAMPLE ANALYSES

Compound	Concentration ppbv	Radian ID
1,3-Butadiene	0.18	1292
Chloroprene	0.46	1286
Trichloroethylene	0.09	1292
1,2-Dichloropropane	1.51	1285
Bromodichloromethane	0.12	1286
n-Octane	0.07	1292
n-Octane	0.46	1309
1,1,2-Trichloroethane	5.06	1310
m-Dichlorobenzene	0.04	1309

TABLE 8-9. COMPOUND IDENTIFICATION CONFIRMATION

GC/MD versus GC/MS comparison	Cases	Percentage
Positive GC/MD - Positive GC/MS	29	27.62
Positive GC/MD - Negative GC/MS	2	1.90
Negative GC/MD - Positive GC/MS	10	9.52
Negative GC/MD - Negative GC/MS	<u>64</u>	<u>60.95</u>
Total	105	99.99%

Total compound identification confirmation = 27.62% + 60.95% = 88.57%

8.8 DATA RECORDS

Data records for the 3-hour air toxics samples include:

- NMOC concentration of the sample;
- Copies of the gas chromatographic trace for FID, PID, and ECD;
 - Response data on Bernoulli disk;
 - Retention time for each compound; and
 - Area counts for each detector.

In addition, daily calibration response factors are recorded on magnetic disk along with the retention time and area counts for each compound in the standard.

9.0 RECOMMENDATIONS, THREE-HOUR AIR TOXICS PROGRAM

The following recommendations derive from the 3-hour Air Toxics Monitoring Program. The studies (Sections 9.1 and 9.2) are directed toward areas in which additional information is needed to validate further the air toxics results.

9.1 COMPOUND STABILITY STUDIES

Compound stability in this context refers to whether the apparent concentration of a compound in a sample taken from a canister is changing over time. The apparent change in concentration may result from a chemical reaction of the compound while it is in the canister, or result from a change in the gas phase concentration caused by adsorption of the compound on the interior canister surfaces.

A study needed to investigate this phenomenon would take several canisters--at least three from each initial concentration--ranging in target compound concentration from zero to 20 ppbv. The canisters would be analyzed 24 hours after mixing, 72 hours after mixing, 30 days after mixing, and 60 days after mixing to determine any concentration changes. It is also recommended that the same concentrations be mixed in canisters, but that equilibration times of 7 days and 30 days be assigned before the first samples are drawn from the canisters to determine the effect of equilibration time on the concentration samples withdrawn from the canisters.

9.2 CANISTER CLEANUP STUDIES

The present canister cleanup procedure has not been studied in sufficient detail to determine the amount of carryover for each of the air toxics compounds. Experience has shown^{4,10,11} that the present cleanup procedure is satisfactory so long as a period less than a week elapses between sampling and analysis.

A study needs to be conducted to determine the effects of:

- Additional pressurization/vacuum cycles on cleanup;
 - Heating the canisters during cleanup;
 - Vacuum holding time during cleanup; and
 - Holding time between cleanup and sampling
- on the carryover for each air toxics target compound.

The present canister cleanup procedure is described in Section 3.3.2 and consists of three vacuum/pressurization cycles with cleaned, dried air that has been humidified. These cycles are followed by a final vacuum step to 5 mm Hg vacuum. Preliminary measurements¹¹ have indicated that after this cleaning procedure has been completed, there may be sufficient organic compounds still adsorbed on the canister interior surfaces to be desorbed and measured in the 0.05 to 0.50 ppbv range, especially for holding times of 7 days, 14 days, and 28 days.

9.3 CARBONYL STUDIES

Recommendations for carbonyl samples are already referred to in Section 6.7. Sections 6.1, 6.2, 6.3, 6.4, and 6.5 would also apply to carbonyl sampling.

10.0 CARBONYL SAMPLING, ANALYSIS, AND QUALITY ASSURANCE PROCEDURES

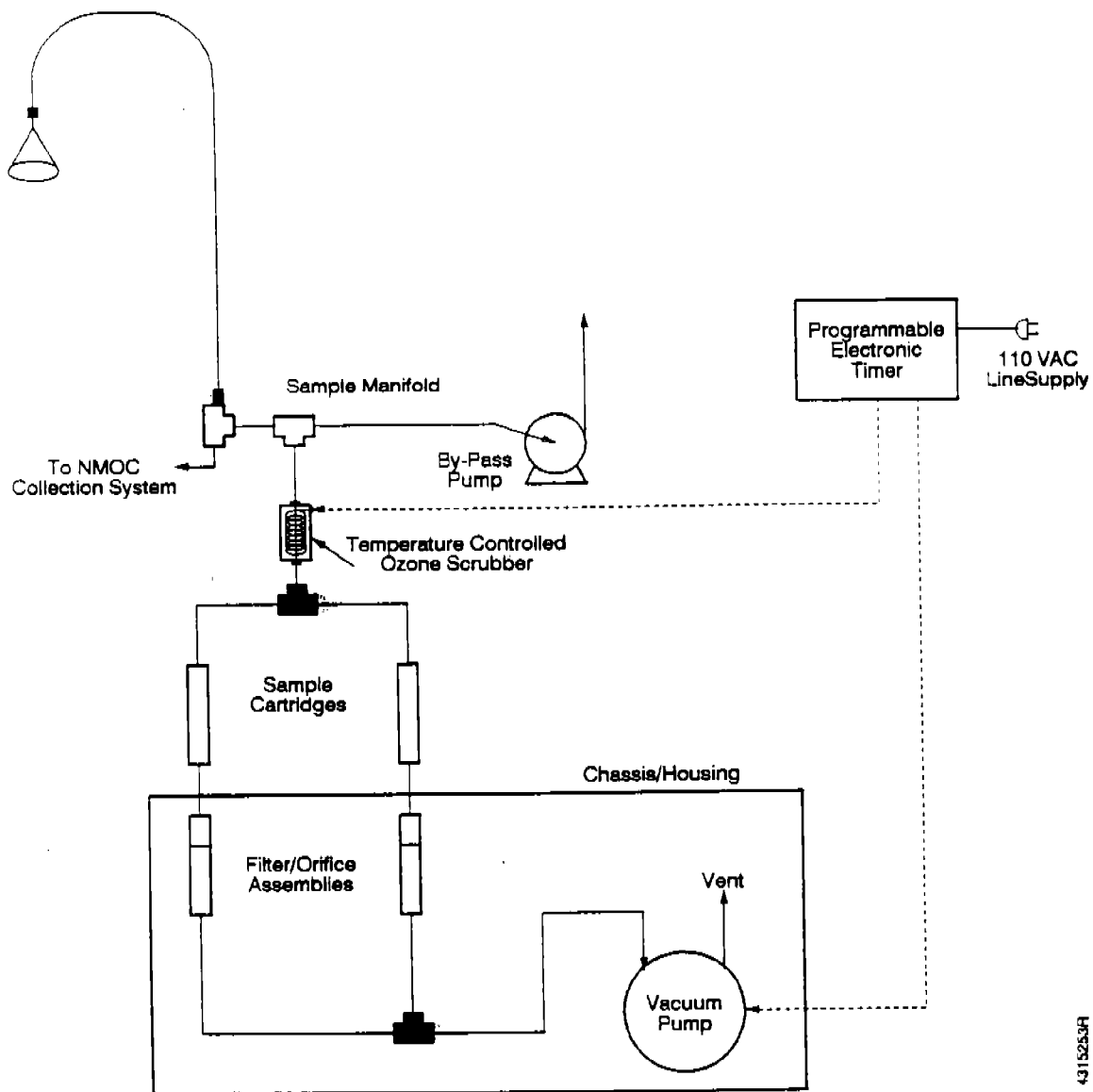
Sampling and analysis procedures for the carbonyl samples, along with the quality assurance procedures used to quantify data quality are described in this section. The site operator's task involved recognizing problems with sampling equipment and procedures, and notifying Radian personnel at Research Triangle Park so that appropriate corrective action might be taken.

10.1 SAMPLING EQUIPMENT AND PROCEDURES

A schematic diagram of a typical carbonyl sampler is shown in Figure 10-1. The 3-hour carbonyl sample subsystem collects a discrete sample through the use of a control system that is common with the NMOC system. Ambient air was drawn through the carbonyl sampler cartridges from a glass manifold. The ambient air was introduced through a short section of chromatographic-grade stainless steel tubing into an ozone scrubber column. The scrubber column was maintained at 200°F to prevent moisture condensation. Before entering the carbonyl cartridges, the ambient air samples flowed through an ozone scrubber, or denuder. The carbonyl cartridges are mounted in parallel, so that the carbonyl samples are collected in duplicate during each sample collection period. The carbonyl cartridge is a commercially available (Waters Co.) silica gel Sep-Pak® cartridge which is coated with 2,4-dinitrophenol hydrazine (DNPH). The cartridges are prepared in batches by the laboratory and stored under refrigeration until shipped to the field.

The carbonyl cartridges are installed in the sample line one day prior to scheduled sample collection. A 3-hour sample collection period was utilized for both the canister and cartridge samples. In addition to the carbonyl cartridges installed in the sample line, a third cartridge is sent along in the shipment box as a trip blank or spare cartridge.

The flow rate through each sample cartridge was measured before and after each collection period by the site operator. The flow rate was measured with a calibrated rotameter and recorded on a preformatted data sheet. The volume of ambient air sampled through each cartridge was calculated in the laboratory based on the field-recorded flow rate measurements.



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Figure 10-1. 3-Hour carbonyl sampling subsystem.

10.2 ANALYTICAL PROCEDURES

The analytical procedures for aldehydes are given below. Sample preparation and analyses are performed at the Radian PPK laboratory. A sample cartridge is removed from its shipping vial and attached to the end of a 10-mL polypropylene syringe. Four milliliters of acetonitrile are added to the syringe and allowed to drain through the cartridge into the graduated centrifuge tube. After the drainage has stopped the volume of extract is made up to 4-mL with acetonitrile and mixed. This solution is transferred to a 4-mL sample vial fitted with a Teflon®-lined self-sealing septum and stored in a refrigerator until used. TO-11 high pressure liquid chromatography (HPLC) column and elution solvents used for analysis were modified to decrease analysis time.

The separation is done using a 25 cm x 4.6 mm C18 analytical column with 5-micron particle size. Typically 50-microliter samples are injected with an automatic sample injector. The following gradient elution is carried out at 0.9 mL/min:

<u>Time (Min.)</u>	<u>% Water</u>	<u>% Acetonitrile</u>	<u>% Methanol</u>
0	40	20	40
5	25	5	70
15	15	5	80
21	15	5	80
23	40	20	40
33	40	20	40

Detector signals from a multiwavelength detector are collected for 30 minutes at 360 nanometers (nm). Any residual sample is eluted from the column in two minutes with a 50:50 mixture of water and acetonitrile.

The relevant chromatographic peaks determined by acceptable retention times are integrated and the concentrations calculated using standard curves. Detection limits are determined by a one-sided tolerance interval around the repeatability of the lowest standard. The analysis optimized sample throughput for analysis of formaldehyde, acetaldehyde, acrolein, acetone, methylethylketone, butyraldehyde, isobutyraldehyde, propionaldehyde, benzaldehyde, tolualdehyde, and dimethylbenzaldehyde. Some other species may

coelute with these target compounds using this HPLC column and gradient elution approach.

Aldehyde species reported are formaldehyde and acetaldehyde. Acetone, a ketone, is also reported. All results were reported in parts per billion by volume (ppbv). All Radian reported analyses were identified by the unique tube numbers which were recorded on the preformatted field data sheets.

10.3 QUALITY ASSURANCE PROCEDURES

Quality assurance procedures relative to calibration data for acetone, formaldehyde, and acetaldehyde are discussed below. Daily quality control procedures are also discussed. Sampling and analysis precision was determined from the analysis of duplicate field samples and duplicate laboratory analyses. Sample custody records were maintained throughout the program. Figure 10-2 shows the multipage field data and custody sheet used for the carbonyl cartridges.

10.4 CALIBRATION PROCEDURES

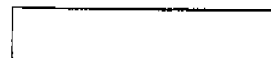
The calibration procedures used for this study followed Radian standard operating procedures.

10.4.1 Daily Quality Control Procedures

Daily calibration checks were used to assure that the analytical procedures were in control. About 100 tubes were analyzed for aldehydes. Daily QC checks were performed each day analyses were conducted.

10.4.2 Duplicate Samples

Duplicate field cartridges were installed in parallel in the sample probe for each sampling episode, as shown in Figure 10-1. The paired average of the analyses of these duplicate cartridges was used as the average sample concentration in this report. If one of the field duplicates was broken or otherwise declared invalid, the analysis of the remaining cartridge was used as the reported sample concentration. Likewise if one of the duplicates showed a concentration above the detection limit and the other duplicate reported a concentration below the detection limit, the concentration above the detection limit was reported as the sample concentration.



URBAN TOXICS MONITORING PROGRAM

Aldehyde Data Sheet

City _____ Sample Date _____
 SAROAD No. _____ A05 Sampler No. _____

Cartridge	Scrubbed	Unscrubbed	Blank
Tube No.	R _____ G _____	R _____ G _____	_____
Lot No.	_____	_____	_____
Rotameter No. _____			
Rotameter Reading ¹ _____ / _____ (before)	Flow Rate ²		LPM
Rotameter Reading ¹ _____ / _____ (after)	Before		_____
Sampling Time/Duration _____ (hours)	After		_____
Sampling Volume ³ _____ (liters)	Average		_____
Average Ambient Temperature _____ (C° or F°)			
Average Barometric Pressure _____ (mm Hg)			
Site Operator _____			
Comments/Remarks _____			

Sample Control Copy

¹ Rotameter reading center of black ball.
² Calculated from calibration curve by the laboratory.
³ Calculated by laboratory.

3003885R

Figure 10-2. Field data and custody form.

10.4.3 Trip Blanks

For each pair of aldehyde samples, a trip-blank cartridge was included in the field site shipment. The blank consisted of a regular DNPH-cartridge with caps, identical with the sample cartridges. Each cartridge had a unique serial number for identification purposes. The blank cartridge accompanies the duplicate sample cartridges on the trip to and from the site, without removing the caps on each end of the cartridge. The trip-blank cartridge is not exposed to air at any time during the shipment or sampling periods. The trip-blank cartridges are analyzed for aldehydes at the same time the sample cartridges are analyzed. The purpose of the trip blank was to assess the potential for field trip contamination. The results are not blank corrected.

10.4.4 Precision

Precision was measured as the average standard deviation of the paired duplicate samples. The relation between precision and mean concentration, and between absolute percent difference and mean concentration were investigated. Percent differences for formaldehyde gives a measure of the precision of the sampling and analysis from the pairs of carbonyl cartridges samples with each ambient air samples. Sampling and analytical error ranged from -61.4% to 103.0, averaging 0.35% overall, with a standard deviation of the percent differences equal to 46.5 ppbv.

10.4.5 Practical Quantitation Limit

Approximate values for the Practical Quantitation limits (PQLs) are given in Table 10-1 for the carbonyls of interest in this study. PQLs for formaldehyde, acetaldehyde, valeraldehyde, hexaldehyde, and benzaldehyde were estimated experimentally. PQLs for the other compounds in Table 10-1 were estimated from the DNPH derivative of formaldehyde.

10.5 RESULTS

Analytical results of ambient air samples for carbonyl compounds at Baton Rouge, LA (BRLA); Newark, NJ (NWNJ); and Plainfield, NJ (PLNJ) are given in Tables 10-2 through 10-4. The tables give the sampling date, the Radian sample ID, sample tube serial number, the formaldehyde and acetaldehyde concentrations in ppbv, and the percent difference for the pair of carbonyl cartridges taken with each ambient air sample (Radian ID Number). No carbonyl

TABLE 10-1. PRACTICAL CARBONYL QUANTITATION LIMIT^a

Compound	PQL (ppbv)
Formaldehyde	0.81
Acetaldehyde	0.71
Acrolein	0.71
Acetone	0.71
Propionaldehyde	0.71
Butyraldehyde	0.67
Isobutyraldehyde	0.67
Methylethylketone	0.67
Valeraldehyde	0.60
Isovaleraldehyde	0.36
Hexaldehyde	0.57
Benzaldehyde	0.57
o-Tolualdehyde	0.57
m-Tolualdehyde	0.57
p-Tolualdehyde	0.57
Dimethylbenzaldehyde	0.55

^aPractical Quantitation Limit (PQL) assumes at least a 140-L gas (air) sample.

TABLE 10-2. CARBONYL RESULTS FOR BATON ROUGE, LA (BRLA)

Sampling Date	Radian Sample ID	Tube Number	Concentration		Formaldehyde Percent Difference
			Formaldehyde (ppbv)	Acetaldehyde (ppbv)	
08/10/90	1384	26E	7.9	a	27.4
08/10/90	1384	47M	10.5	a	
		Average	9.2		
08/14/90	1386	51D	4.7	a	74.7
08/14/90	1386	53F	10.4	1.48	
		Average	7.6		
08/16/90	1406	133M	2.2	a	
08/16/90	1406	152J	b	a	
		Average	2.2		
08/20/90	1416	111M	b	a	
08/20/90	1416	127E	2.2	a	
		Average	2.2		
08/22/90	1430	18J	12.8	a	-6.5
08/22/90	1430	39E	12.0	a	
		Average	12.4		
08/24/90	1437	44J	4.4	a	-53.4
08/24/90	1437	52E	2.5	a	
		Average	3.5		
08/28/90	1466	19K	4.6	a	-31.1
08/28/90	1466	38D	3.3	a	
		Average	3.9		
08/30/90	1478	37C	2.1	a	-13.5
08/30/90	1478	50C	1.8	a	
		Average	1.9		
09/05/90	1500	24C	9.7	a	22.3
09/05/90	1500	25D	12.1	a	
		Average	10.9		
09/07/90	1519	11C	13.2	a	-3.6
09/07/90	1519	20L	12.8	a	
		Average	13.0		
09/11/90	1533	15G	3.2	a	31.7
09/11/90	1533	49B	4.4	a	
		Average	3.8		
Average =					5.3
Std. Dev. =					38.1

a Below detection limit of 0.71 ppbv.

b Quality assurance cartridge used to determine percent recovery for formaldehyde spike.

TABLE 10-3. CARBONYL RESULTS FOR NEWARK, NJ (NWNJ)

Sampling Date	Radian Sample ID	Tube Number	Concentration		Formaldehyde Percent Difference
			Formaldehyde (ppbv)	Acetaldehyde (ppbv)	
08/06/90	1648	67G	3.3	a	-3.8
08/06/90	1648	63C	3.1	a	
		Average	3.2		
08/08/90	1371	66F	9.8	a	-7.3
08/08/90	1371	70L	9.1	a	
		Average	9.5		
08/10/90	1380	69K	4.3	a	-32.4
08/10/90	1380	65E	3.1	a	
		Average	3.7		
08/14/90	1391	107G	1.8	a	103.0
08/14/90	1391	105E	5.6	a	
		Average	3.7		
08/16/90	1412	77F	b	a	
08/16/90	1412	108J	4.5	a	
		Average	4.5		
08/20/90	1415	149E	b	a	
08/20/90	1415	170D	1.3	a	
		Average	1.3		
08/22/90	1429	174J	0.9	a	-19.0
08/22/90	1429	176L	0.5	a	
		Average	0.7		
08/24/90	1446	103C	1.2	a	63.6
08/24/90	1446	110L	2.3	a	
		Average	1.7		
08/28/90	1461	169C	1.3	a	-55.1
08/28/90	1461	167A	0.8	a	
		Average	1.0		
08/30/90	1484	172F	1.3	a	0.8
08/30/90	1484	173A	1.3	a	
		Average	1.3		
Average =					7.5
Std. Dev. =					57.4

a Below detection limit of 0.71 ppbv.

b Quality assurance cartridge used to determine percent recovery of formaldehyde spike.

TABLE 10-4. CARBONYL RESULTS FOR PLAINFIELD, NJ (PLNJ)

Sampling Date	Radian Sample ID	Tube Number	Concentration		Formaldehyde Percent Difference
			Formaldehyde (ppbv)	Acetaldehyde (ppbv)	
08/06/90	1350	22A	a	b	-61.40
08/06/90	1350	23B	1.4	b	
		Average	1.4		
08/08/90	1361	83B	a	b	
08/08/90	1361	83A	2.9	b	
		Average	2.9		
08/10/90	1377	90J	1.7	b	
08/10/90	1377	89G	0.9	b	
		Average	1.3		
08/14/90	1397	13E	a	b	
08/14/90	1397	14F	1.5	b	
		Average	1.5		
08/16/90	1403	113B	a	b	
08/16/90	1403	118G	a	b	
		Average	a		
08/20/90	1442	130J	c	b	
08/20/90	1442	131K	a	b	
		Average	a		
08/22/90	1444	171E	c	b	
08/22/90	1444	125C	2.1	b	
		Average	2.1		
08/24/90	1450	122M	0.9	b	
08/24/90	1450	112A	a	b	
		Average	0.9		
08/28/90	1460	79J	1.7	b	
08/28/90	1460	76E	a	b	
		Average	1.7		
08/30/90	1491	117F	a	b	
08/30/90	1491	120K	a	b	
		Average	a		
				Average =	-61.40

a Below detection limit of 0.81 ppbv.

b Below detection limit of 0.71 ppbv.

c Quality assurance cartridge used to determine percent recovery of formaldehyde spike.

was detected in any of the samples other than formaldehyde and acetaldehyde, as shown.

The results from the field sites are presented as individual and mean concentrations for the 3-hour sample period. The concentration variability and sample population preclude the use of a site mean concentration. The average percent difference in formaldehyde for BRLA and NWNJ are within the expected range of results based on historical data. The higher percent difference (-61%) is due to limited statistical input which result from lower than expected formaldehyde concentrations.

Measures of analytical precision for formaldehyde are given in Table 10-5. For the samples shown in Table 10-5, the analytical precision ranged from -57.7% to 47.0%, averaging -5.4 percent difference. The replicate analysis performed in the laboratory was performed on 10% of the field sample population, covering the range of formaldehyde concentrations. The quality control check of analytical precision indicates that the analysis was in control during the program.

10.5.1 Formaldehyde Control Standards

As a quality control (QC) procedure on the analytical results for formaldehyde, a solution of known concentration was formulated. Throughout the period of time that analyses were performed, QC samples were analyzed on the dates indicated in Table 10-6. As shown in the table, the percent of formaldehyde recovered is shown to range from 85.3 to 114.3, averaging 100.3 percent. These results shown that the analytical technique was consistently good.

10.5.2 Recoveries of Spikes

Three types of spikes were used as quality control procedures:

- (1) Known amounts of formaldehyde were spiked onto DNPH cartridges and then analyzed. These were called laboratory spikes because all of the procedures were performed in the laboratory. Laboratory spike percent recoveries are tabulated in Table 10-7.
- (2) Known amounts of formaldehyde were spiked on DNPH cartridges. The cartridges were taken to the field and used as one of the pair of cartridges during a regular sample collection. The pair of cartridges were returned to the laboratory for analysis. The amount of spike recovered from the spiked cartridges was calculated as a percent recovery using the formaldehyde found on the unspiked cartridge to correct the total formaldehyde found

TABLE 10-5. CARBONYL LABORATORY REPLICATES

Site Code	Radian ID	Tube Number	Formaldehyde		Acetaldehyde Concentration (ppbv)
			Concentration (ppbv)	Percent Difference (%) ^a	
NWNJ	1412	108J	4.5	-55.9	< 0.71
NWNJ	1412		2.5		< 0.71
BRLA	1478	50C	1.8	-16.8	< 0.71
BRLA	1478		1.5		< 0.71
NWNJ	1391	102B	1.4 ^b	47.0	< 1.0 ^b
NWNJ	1391		2.2 ^b		< 1.0 ^b
Lab	Blank	139F	2.0 ^b	-57.7	< 1.0 ^b
Lab	Blank		1.1 ^b		< 1.0 ^b
NWNJ	1461	169C	1.3	17.3	< 0.71
NWNJ	1461		1.6		< 0.71
BRLA	1406	133M	2.2	10.5	< 0.71
BRLA	1406		2.4		< 0.71
NWNJ	1429	176L	0.5	-18.2	< 0.71
NWNJ	1429		0.5		< 0.71
NWNJ	1648	67G	3.3	30.5	< 0.71
NWNJ	1648		4.4		< 0.71
Average =				-5.4	

^a Percent difference = $((\text{Concentration2} - \text{Concentration1}) / ((\text{Concentration2} + \text{Concentration1}) / 2)) * 100$.

^b Blank ug presented because no volume for blanks.

TABLE 10-6. ANALYSIS OF QUALITY CONTROL STANDARDS

Analysis Date	Formaldehyde Concentration (ng/uL)	Percent Of Target ^a
09/28/90	5.19	106.1
09/28/90	4.93	100.9
10/15/90	5.16	105.6
10/15/90	4.17	85.3
10/16/90	4.99	102.0
10/16/90	4.42	90.4
10/16/90	5.30	108.5
10/27/90	5.16	105.6
10/27/90	4.88	99.8
11/12/90	4.66	94.9
11/27/90	5.61	114.3
12/03/90	4.45	90.6
Average =		100.3

^a Known concentration is 4.9 ng/uL.

TABLE 10-7. FORMALDEHYDE LABORATORY SPIKES

Analysis Date	Tube Number	Formaldehyde Concentration (ug)	Percent of Target (%)
09/29/90	138E	25.13	123.2 ^a
10/15/90	144M	17.11	83.9
10/15/90	155M	22.37	109.6
10/16/90	129G	21.30	104.4
10/16/90	134A	25.21	123.6 ^a
10/16/90	140C	20.09	98.5
10/16/90	153K	19.29	94.5
10/26/90	151G	23.94	117.4
10/26/90	237D	24.10	118.1
10/27/90	135B	22.80	111.8
10/27/90	146B	19.56	95.9
10/28/90	136C	20.77	101.8
10/28/90	214Q	22.78	111.7
11/12/90	249R	23.21	113.8
11/13/90	143L	23.07	113.1
11/14/90	145A	16.08	78.8 ^a
11/14/90	154L	17.86	87.6
11/14/90	242K	23.36	114.5
11/27/90	150F	19.62	96.2
		Average =	105.2

^a Outside of desired +/- 20% window.

on the spiked cartridge. Three spiked sample pairs were termed field spikes. The results of percent recovery for field spikes is shown in Table 10-8.

- (3) Carbonyl spikes were formulated by the following procedure. Four silica gel cartridges, previously coated with DNPH, were spiked in the laboratory with formaldehyde, acetaldehyde, and acetone at the following levels: Formaldehyde 20.5 μg ; Acetaldehyde 20.5 μg ; and Acetone 15.1 μg . The spiked cartridges were then processed through the regular extraction - analytical procedure as the other samples. Percent recoveries were calculated and are shown in Table 10-9.

Recoveries of the carbonyl spikes ranged from 88.2% to 110% for formaldehyde; 87.5% to 94.1% for acetaldehyde; and 121% to 134% for acetone. The recoveries for acetone were noticeably higher than the recoveries for formaldehyde and acetaldehyde. Such a result can be explained because of the high probability of contamination from acetone in the laboratory environment.

Average recovery of formaldehyde laboratory spikes was 105.2 percent. Average recovery of formaldehyde field spikes was 115 percent. Both these recovery statistics reflect excellent sampling and analysis procedures.

10.5.3 Blanks

Laboratory blank analysis are summarized in Table 10-10, and field blank results are summarized in Table 10-11. Four out of seven laboratory blanks showed formaldehyde values greater than 1.00 μg , while 19 out of 31 field blanks showed concentrations of formaldehyde greater than 1.00 μg . An acetaldehyde concentration greater than 1.00 μg was indicated in only one field blank from NWNJ. Acetone was detected in one field blank from PLNJ. The reported field concentration were not blank corrected. The significance of measurable formaldehyde deviations in some of the field and laboratory blanks required further investigation.

TABLE 10-8. FIELD SPIKE RECOVERIES OF FORMALDEHYDE

Site Code	Sample Date	Sample ID	Tube Number	Percent Recovery (%) ^a
BRLA	08/16/90	1406	152J	121.4
BRLA	08/16/90	1406	133M	
BRLA	08/20/90	1416	111M	157.6
BRLA	08/20/90	1416	127E	
NWNJ	08/16/90	1412	77F	94.5
NWNJ	08/16/90	1412	108J	
NWNJ	08/20/90	1415	149E	108.3
NWNJ	08/20/90	1415	170D	
PLNJ	08/20/90	1442	130J	130.3
PLNJ	08/20/90	1442	131K	
PLNJ	08/22/90	1444	171E	92.9
PLNJ	08/22/90	1444	125C	
Average				117.5

^a Percent Recovery = (Recovered ug from Spiked Cartridge - Recovered ug from Unspiked Cartridge)/20.46*100

TABLE 10-9. CARBONYL SPIKE RECOVERIES

Cartridge Number	Formaldehyde Recovery (%)	Acetaldehyde Recovery (%)	Acetone Recovery (%)
1	110.6	87.5	121.6
2	110.0	94.0	134.3
3	88.2	89.2	126.8
4	91.8	94.1	131.4

TABLE 10-10. CARBONYL LABORATORY BLANKS

Analysis Date	Tube Number	Concentration	
		Formaldehyde (ug)	Acetaldehyde (ug)
10/04/90	31J	< 1.0	< 1.0
10/13/90	137D	< 1.0	< 1.0
10/13/90	36B	1.08	< 1.0
10/16/90	329	< 1.0	< 1.0
10/26/90	234A	4.52	< 1.0
11/11/90	142K	1.56	< 1.0
11/27/90	139F	2.01	< 1.0

TABLE 10-11. CARBONYL FIELD BLANKS

Site Code	Sampling Date	Sample ID	Tube Number	Formaldehyde Derivative Concentration (ug)	Acetaldehyde Derivative Concentration (ug)	Acetone Derivative Concentration (ug)
BRLA	08/10/90	1384	59L	2.97	<1.00	<1.00
	08/14/90	1386	52K	2.27	<1.00	<1.00
	08/16/90	1406	128F	2.14	<1.00	<1.00
	08/20/90	1416	132L	3.01	<1.00	<1.00
	08/22/90	1430	10B	<1.00	<1.00	<1.00
	08/24/90	1437	45K	<1.00	<1.00	<1.00
	08/28/90	1466	35A	1.80	<1.00	<1.00
	08/30/90	1478	41G	1.73	<1.00	<1.00
	09/05/90	1500	27F	2.65	<1.00	<1.00
	09/07/90	1519	12D	2.18	<1.00	<1.00
	09/11/90	1533	46L	1.13	<1.00	<1.00
NWNJ	08/06/90	1648	61A	1.99	<1.00	<1.00
	08/08/90	1371	64D	<1.00	<1.00	<1.00
	08/10/90	1380	62B	4.46	<1.00	<1.00
	08/10/90	1412	109K	5.21	1.75	<1.00
	08/14/90	1391	102B	1.35	<1.00	<1.00
	08/20/90	1415	168B	<1.00	<1.00	<1.00
	08/22/90	1429	114C	<1.00	<1.00	<1.00
	08/24/90	1446	106F	<1.00	<1.00	<1.00
	08/28/90	1461	104D	3.76	<1.00	<1.00
	08/30/90	1484	175K	<1.00	<1.00	<1.00
PLNJ	08/06/90	1350	33L	<1.00	<1.00	<1.00
	08/08/90	1361	86D	2.33	<1.00	<1.00
	08/10/90	1377	85C	1.49	<1.00	8.70
	08/14/90	1397	21M	1.83	<1.00	<1.00
	08/16/90	1403	121L	1.69	<1.00	<1.00
	08/20/90	1442	123A	<1.00	<1.00	<1.00
	08/22/90	1444	124B	1.80	<1.00	<1.00
	08/24/90	1450	115D	<1.00	<1.00	<1.00
	08/28/90	1460	73B	<1.00	<1.00	<1.00
	08/30/90	1491	116E	<1.00	<1.00	<1.00

•

11.0 REFERENCES

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3. Radian Corporation. 1989 Nonmethane Organic Compound and Three-Hour Air Toxics Monitoring Program. Final Report. Prepared for U. S. Environmental Protection Agency, Research Triangle Park, NC, 27711, EPA-450/4-90-011. May 1990.
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10. McAllister, R. A., Radian Corporation. Letter and Proposal, entitled "Wet Zero Study", to Frank F. McElroy, Quality Assurance Division, Environmental Systems Monitoring Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. November 15, 1988.
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APPENDICES

APPENDIX A: SAMPLING SITES FOR 1990 NMOC MONITORING PROGRAM

**APPENDIX B: CRYOGENIC PRECONCENTRATION AND DIRECT FLAME
IONIZATION DETECTION (PDFID) METHOD**

APPENDIX C: 1990 NMOC MONITORING PROGRAM SITE DATA

**APPENDIX D: 1990 NMOC MONITORING PROGRAM INVALIDATED AND MISSING
SAMPLES**

APPENDIX E: PDFID INTEGRATOR PROGRAMMING INSTRUCTIONS

APPENDIX F: 1990 NMOC DAILY CALIBRATION DATA

APPENDIX G: 1990 NMOC IN-HOUSE QUALITY CONTROL SAMPLES

APPENDIX H: MULTIPLE DETECTOR SPECIATED THREE-HOUR SITE DATA SUMMARIES

Page 1

APPENDIX A
SAMPLING SITES FOR 1990 NMOC MONITORING PROGRAM

TABLE A-1. 1990 NMOC AND THREE-HOUR AIR TOXICS MONITORING PROGRAM SITES.

Site No.	U.S. EPA Region	City	Radian Site Code	AIRS Number	3-Hr Air Toxics
1	I	East Hartford, CT	HTCT	09-003-1003	No
2	II	Hempstead, NY (Eisenhower Park, Long Island)	LINY	36-059-0005	No
3		New York, NY (Mabel Dean)	MNY	36-061-0010	Yes
4		Newark, NJ (St. Charles St)	NWNJ	34-013-0011	Yes
5		Plainfield, NJ	PLNJ	34-035-1001	Yes
6	VI	Beaumont, TX (Lamar U)	BMTX	48-245-0009	No
7		Baton Rouge, LA	BRLA	22-033-0904	Yes

EPA AEROMETRIC INFORMATION RETRIEVAL SYSTEM (AIRS)
AIR QUALITY SUBSYSTEM
SITE DESCRIPTION INVENTORY

DATE 11/13/90
AMP380

STATE (09): CONNECTICUT

EPA-REGION: 01

SITE ID : 09-003-1003 CITY (22630): EAST HARTFORD
CITY POPULATION : 52,503 COUNTY (045): HARTFORD CO
ACK POPULATION : 3,372,067 ADDR (042): HARTFORD-NEW HAVEN-SPRINGFIELD
DATE ESTABLISHED: 81/01/01 LAND USE (10): RESIDENTIAL
DATE TERMINATED : / / LOCATION SETTING (2): SUBURBAN
SITE ADDR: 30 REMINGTON ROAD
URBAN AREA (3280): HARTFORD, CT
SUPPORTING AGENCY (001): CONNECTICUT DEPARTMENT OF ENVIRONMENTAL PROTECTION
COMMENTS: MAIN ST AND REMINGTON RD, SENIOR CITIZEN'S CENTER
SITE-USER-INFO: 03 = POP, NEIGH., NO2 = HIGH CONC. NEIGH., HC DISC 1982

PARAMETER : 42601 ATTAIN-STATUS :
POC : ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 81/01/01 REPORT-ORG :
REF-METHOD : NO-EFFECT-DATE : / /
REF-METH-DATE : / /
MONITOR-COMMENTS : 14

PARAMETER : 42602 ATTAIN-STATUS :
POC : ANALYZ-LAB :
MONITOR-TYPE : 2 COLLECT-LAB :
MT-EFF-DATE : 81/01/01 REPORT-ORG : 901
REF-METHOD : NO-EFFECT-DATE : 81/04/01
REF-METH-DATE : / /
MONITOR-COMMENTS : 14

PARAMETER : 42603 ATTAIN-STATUS :
POC : ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 81/01/01 REPORT-ORG :
REF-METHOD : NO-EFFECT-DATE : / /
REF-METH-DATE : / /
MONITOR-COMMENTS : 14

PARAMETER : 43102 ATTAIN-STATUS :
POC : ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 81/01/01 REPORT-ORG : 908
REF-METHOD : NO-EFFECT-DATE : 81/01/01
REF-METH-DATE : / /
MONITOR-COMMENTS : 14

PARAMETER : 43102 ATTAIN-STATUS :
POC : ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 81/01/01 REPORT-ORG : 908
REF-METHOD : NO-EFFECT-DATE : 81/01/01
REF-METH-DATE : / /
MONITOR-COMMENTS : 14

MONITOR-COMMENTS : SPECIAL STUDY OF NON-METHANE ORGANIC COMPOUND

LATITUDE : 4147108 N UTM EASTING : 696855
LONGITUDE : 72137152 W DIFF. GMT : 05
UTM ZONE : 18 ELEVATION ABOVE NAD : 15 M
UTM NORTHING : 4628466 RECORD LAST UPDATED : 90/03/22
HW EVAL DATE : 82/09/29 LAST HW EVAL : / /
DISTANCE CITY: 005 COMPASS SECTOR : NE
HC IND: Y NET DATA : N

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-ORG :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 4 M

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-ORG :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 4 M

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-ORG :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 4 M

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-ORG :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 4 M

DATE 11/13/90
AMP380

EPA AEROMETRIC INFORMATION RETRIEVAL SYSTEM (AIRS)
AIR QUALITY SUBSYSTEM
SITE DESCRIPTION INVENTORY

PAGE 4

EPA-REGION: 02

STATE (36): NEW YORK

SITE ID : 36-059-0005 CITY (13159): HEMPSTEAD
CITY POPULATION : 40,404 COUNTY (059): NASSAU CO
ACQ# POPULATION : 16,525,701 ACR# (043): NEW JERSEY-NEW YORK-CORRECTION
DATE ESTABLISHED : / / LAND USE (2): COMMERCIAL
DATE TERMINATED : / / LOCATION SETTING (2): SUBURBAN
SITE ADDR1 EISENHOWER PARK, MERRICK AVENUE COUNTRY H
URBAN AREA (0000): NOT IN AN URBAN AREA
SUPPORTING AGENCY (000): ***** DESCRIPTION UNKNOWN *****
COMMENTS: NYS #2950-10 START 502,01,03, 012, TSP171, PM1072, NECRMPT180, NO, NO2, O3
SITE-USEH-INF01 03-#334105002F01 12/82, MIDDLE SCALE, MEETS SITTING, NO2-2-025 - 12/86

PARAMETER : 11101 ATTAIN-STATUS :
POC : 1 ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 70/01/01 REPORT-ORG :
REF-METHOD : / / R0-EFFECT-DATE : 83/01/01
REF-METH-DATE : / / ACT-TAKEN/REASON :
MONITOR-COMMENTS : 91

PARAMETER : 11101 ATTAIN-STATUS :
POC : 1 ANALYZ-LAB :
MONITOR-TYPE : 2 COLLECT-LAB :
MT-EFF-DATE : 01/01/01 REPORT-ORG :
REF-METHOD : / / R0-EFFECT-DATE : 83/01/01
REF-METH-DATE : / / ACT-TAKEN/REASON :
MONITOR-COMMENTS : 91

PARAMETER : 11103 ATTAIN-STATUS :
POC : 1 ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 75/01/01 REPORT-ORG :
REF-METHOD : / / R0-EFFECT-DATE : / /
REF-METH-DATE : / / ACT-TAKEN/REASON :
MONITOR-COMMENTS : 91

PARAMETER : 11201 ATTAIN-STATUS :
POC : 1 ANALYZ-LAB :
MONITOR-TYPE : 0 COLLECT-LAB :
MT-EFF-DATE : 75/01/01 REPORT-ORG :
REF-METHOD : / / R0-EFFECT-DATE : / /
REF-METH-DATE : / / ACT-TAKEN/REASON :
MONITOR-COMMENTS : 91

LATITUDE : 40:44:43 N UTM EASTING : 619300
LONGITUDE : 73:55:13 W DIFF. GMI : 05
UTM ZONE : 18 ELEVATION ABOVE MSL : 27 M
UTM NORTHING : 4511200 RECORD LAST UPDATED : 8/06/14
NO EVAL DATE : / / LAST NEW EVAL : / /
DISTANCE CITY : COMPASS SECTION :
UTM IND1 : MET DATA :
MSA (5380): NASSAU-SUFFOLK, NY

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 5 M

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 5 M

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 5 M

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT : 5 M

EPA AIRBORNE INFORMATION RETRIEVAL SYSTEM (AIRS)

AIR QUALITY SUBSYSTEM
SITE DESCRIPTION INVENTORY

DATE 11/02/87
AIR300

STATE 1361: NEW YORK

LPA REGION: 02

LATITUDE : 40:44:22 N UTM EASTING : 585607
LONGITUDE : 73:59:10 W DIFF. GMT : 05
UTM ZONE : 18 ELEVATION ABOVE MSL : 38 M
UTM NORTHING : 4510116 RECORD LAST UPDATED: 89/10/26
UTM EVAL DATE: 80/09/23 LAST REQ EVAL : 80/09/22
DISTANCE CITY: 003 COMPASS SECTOR : S
IC IND: Y NET DATA : Y
HSA (5600): NEW YORK, NY

SITE ID : 36-061-0010 CITY (51000): NEW YORK CITY
CITY POPULATION : 7,071,639 COUNTY (061): NEW YORK CO
ACQR POPULATION : 16,525,701 ACQR (043): NEW JERSEY-NEW YORK-CONNECTICU
DATE ESTABLISHED: / / LAND USE (1): RESIDENTIAL
DATE TERMINATED: / / LOCATION SETTING (1): URBAN AND CENTER CITY
SITE ADDR: LABEL DEAN HIGH SCH. ANNEX, 240 2ND AVE.
URBAN AREA (5601): NEW YORK, NY-NORTHEASTERN NJ
SUPPORTING AGENCY (001): NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVA
COMMENTS: NYSH7093-05, START 102.03 11/10/76, TSP 10/10, CO 10/3/77, SO2 2/5/78
SITE-USER-INFO: 1980 RECRIP, DISC. CO, 03 5/25, RESIART 03 9/24/82, 1ELEV. TSP 102.

PARAMETER : 43102 ATTAIN-STATUS : 908
POC : 1 ANALYZ-LAB : 908
MONITOR-TYPE : 3 COLLECT-LAB : 908
UT-EFF-DATE : 86/06/02 REPORT-ORG :
REF-METHOD : RO-EFFECT-DATE : / / PROJECT-CLASS :
ACT-TAKEN/REASON:

MONITOR-COMMENTS : SPECIAL STUDY OF PM10 METHANE ORGANIC COMPOUND

PARAMETER : 43102 ATTAIN-STATUS : 908
POC : 2 ANALYZ-LAB : 908
MONITOR-TYPE : 3 COLLECT-LAB : 908
UT-EFF-DATE : 86/06/05 REPORT-ORG :
REF-METHOD : RO-EFFECT-DATE : / / PROJECT-CLASS :
ACT-TAKEN/REASON:

MONITOR-COMMENTS : NON-METHANE ORGANIC COMPOUND SAME DAY DIFFERENT CANTISTER AS POL.

PARAMETER : 43102 ATTAIN-STATUS : 908
POC : 3 ANALYZ-LAB : 908
MONITOR-TYPE : 3 COLLECT-LAB : 908
UT-EFF-DATE : 86/06/05 REPORT-ORG :
REF-METHOD : RO-EFFECT-DATE : / / PROJECT-CLASS :
ACT-TAKEN/REASON:

MONITOR-COMMENTS : NON-METHANE ORGANIC COMPOUND SAME DAY DIFFERENT CANTISTER AS 1

LATITUDE : 40:45:33 N UTM EASTING : 587250
LONGITUDE : 73:57:59 W DIFF. GMT : 05
UTM ZONE : 18 ELEVATION ABOVE MSL : 15 M
UTM NORTHING : 4512310 RECORD LAST UPDATED: 89/10/26
UTM EVAL DATE: / / LAST REQ EVAL : 86/04/25
DISTANCE CITY: 001 COMPASS SECTOR : NE
IC IND: Y NET DATA : N
HSA (5600): NEW YORK, NY

SITE ID : 36-061-0056 CITY (51000): NEW YORK CITY
CITY POPULATION : 7,071,639 COUNTY (061): NEW YORK CO
ACQR POPULATION : 16,525,701 ACQR (043): NEW JERSEY-NEW YORK-CONNECTICU
DATE ESTABLISHED: 85/07/06 LAND USE (1): COMMERCIAL
DATE TERMINATED: / / LOCATION SETTING (1): URBAN AND CENTER CITY
SITE ADDR: PS 59, 208 E. 57TH STREET, MANHATTAN
URBAN AREA (5601): NEW YORK, NY-NORTHEASTERN NJ
SUPPORTING AGENCY (001): NEW YORK STATE DEPARTMENT OF ENVIRONMENTAL CONSERVA
COMMENTS: NYSH7093-10, TSP, PM10 (01001), SO2, NO2 MONITORING

SITE-USER-INFO: SITE TEMPORARILY DISC. 8/06/22, ROOF REPAIRS, NO2 TO UPPER ROOF

DATE 11/02/89
AUP300

LPA AIRBORNE INFORMATION RETRIEVAL SYSTEM (AIRS)
AIR QUALITY SUBSYSTEM
SITE DESCRIPTION INVENTORY

LPA REGION: 02

STATE (34): NEW JERSEY

SITE ID : 34-013-0011 CITY (51000): ELIZABETH
CITY POPULATION : 329,248 COUNTY (013): ESSEX CO
AQR POPULATION : 16,525,701 AQR (043): NEW JERSEY-NEW YORK-CONNECTICU
DATE ESTABLISHED: 85/01/01 LAND USE (13): INDUSTRIAL
DATE TERMINATED : / / LOCATION SETTING (11): URBAN AND CENTER CITY
SITE ADDR: ST. CHARLES BLVDEN ROSSOUTH & KARENHOL ST
URBAN AREA (5601): NEW YORK, NY-NORTHEASTERN NJ
SUPPORTING AGENCY (001): NEW JERSEY STATE DEPARTMENT OF ENVIRONMENTAL PROTECT
COMMENTS: NJ #07142, START 1/1/85, RELOC. FROM 340130000, SITTING CRITERIA?
SITE-USER INFO: PHLO, DICHO, START 3/15/86, ELEV. 16' 103 DOWN 5/10/86-3/25/87

PARAMETER : 43102
POC : 1
MONITOR-TYPE : 3
MT-EFF-DATE : 86/06/02
REF-METHOD : / /
REF-MTH-DATE : / /
MONITOR-COMMENTS : SPECIAL STUDY OF HIGH-METHANE ORGANIC COMPOUND

ATTACH-STATUS : 86/06/02
ANALYZ-LAB : 908
COLLECT-LAB : 908
REPORT-ORG : 908
RO-EFFECT-DATE : / /
RO-EFFECT-DATE : / /
ACT-TAKEN/REASON:

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT :

PARAMETER : 43102
POC : 2
MONITOR-TYPE : 3
MT-EFF-DATE : 86/06/19
REF-METHOD : / /
REF-MTH-DATE : / /
MONITOR-COMMENTS : HIGH METHANE ORGANIC COMPOUND SAME DAY/CANISTER AS POC1

ATTACH-STATUS : 86/06/19
ANALYZ-LAB : 908
COLLECT-LAB : 908
REPORT-ORG : 908
RO-EFFECT-DATE : / /
RO-EFFECT-DATE : / /
ACT-TAKEN/REASON:

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT :

PARAMETER : 43102
POC : 3
MONITOR-TYPE : 3
MT-EFF-DATE : 86/06/06
REF-METHOD : / /
REF-MTH-DATE : / /
MONITOR-COMMENTS :

ATTACH-STATUS : 86/06/06
ANALYZ-LAB : 908
COLLECT-LAB : 908
REPORT-ORG : 908
RO-EFFECT-DATE : / /
RO-EFFECT-DATE : / /
ACT-TAKEN/REASON:

DOMINANT-SOURCE :
MEAS-SCALE :
MONITORING-OBJ :
SITTING-CRITERIA :
SITTING-CRIT-DATE : / /
PROBE-HEIGHT :

SITE ID : 34-035-1001 CITY (59100): PLAINFIELD
CITY POPULATION : 45,555 COUNTY (035): SOMERSET CO
AQR POPULATION : 16,525,701 AQR (043): NEW JERSEY-NEW YORK-CONNECTICU
DATE ESTABLISHED: / / LAND USE (11): RESIDENTIAL
DATE TERMINATED : / / LOCATION SETTING (21): SUBURBAN
SITE ADDR: WEST THIRD AND BURGESS STREETS
URBAN AREA (0001): NOT IN AN URBAN AREA
SUPPORTING AGENCY (000): ***** DESCRIPTION URBAN *****
COMMENTS: NJ #2012, START 5/80, 1980 ME OXIDANT STUDY 03, INDUS02 DISC.5/2/83
SITE-USER INFO: 03 AS A STARS 10/01/84, MEETS SITTING

LATITUDE : 40:43:37 N UTM EASTING : 572280
LONGITUDE : 74:08:39 W DIFF. GMT : 05
UTM ZONE : 18 ELEVATION ABOVE MSL : 18 M
UTM NORTHING : 4494299 RECORD LAST UPDATED: 89/10/26
HQ EVAL DATE: / / LAST REQ EVAL : / /
DISTANCE CITY : COMPASS SECTOR :
HC IND: Y MET DATA :
NSA (5601): MIDDLESEX-SOMERSET-MIDDLESEX, NJ

DATE 02/14/90
ANP300

LPA-REGULATORY

UATMP SITE CODE: BRLA

ENVIRONMENTAL INFORMATION RETRIEVAL SYSTEM (AIRMS)
AIR QUALITY SUBSYSTEM
SITE DESCRIPTION INVENTORY

STATE (22): LOUISIANA

PAGE 5

SITE ID 1 22-053-0000 CITY (05000) EAST BATON ROUGE
CITY POPULATION 1 219,419 COUNTY (053) EAST BATON ROUGE PAR
AOCN POPULATION 1 3,921,500 AOCN (1000) SOUTHERN LOUISIANA-SOUTHEAST 1
DATE ESTABLISHED 1 / / LAND USE (21) COMMERCIAL
DATE TERMINATED 1 / / LOCATION SETTING (13) URBAN AND CENTER CITY
SITE ADDR 1500 RIVERSIDE ROAD
URBAN AREA (0700) BATON ROUGE, LA
SUPPORTING AGENCY (001) LOUISIANA STATE DEPARTMENT OF NATURAL RESOURCES
COMMENT 1

LATITUDE 1 30127134 N UTM EASTING
LONGITUDE 1 91111116 W DIFF. GM 1 60 673989
UTM ZONE 1 15 ELEVATION ABOVE MSL 1 9 M
UTM NORTHING 1 3371065 RECORD LAST UPDATED 1 89/11/22
HW EVAL DATE 1 80/09/10 LAST HW EVAL 1 87/03/25
DISTANCE CITY 1 001 COMPASS SECTOR 1 N
MC IND 1 Y MET DATA 1 N
MSA (0700) BATON ROUGE, LA

APPENDIX B
CRYOGENIC PRECONCENTRATION AND DIRECT FLAME
IONIZATION DETECTION (PDFID) METHOD

COMPENDIUM METHOD T0-12

**DETERMINATION OF NON-METHANE- ORGANIC
COMPOUNDS (NMOC) IN AMBIENT AIR USING
CRYOGENIC PRE-CONCENTRATION AND
DIRECT FLAME IONIZATION DETECTION
(PDFID)**



**QUALITY ASSURANCE DIVISION
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711**

MAY, 1988

METHOD T012

METHOD FOR THE DETERMINATION OF NON-METHANE ORGANIC COMPOUNDS (NMOC)
IN AMBIENT AIR USING CRYOGENIC PRECONCENTRATION AND DIRECT FLAME
IONIZATION DETECTION (PDFID)

1. Scope

- 1.1 In recent years, the relationship between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone has been described by a variety of photochemical dispersion models. The most important application of such models is to determine the degree of control of precursor organic compounds that is necessary in an urban area to achieve compliance with applicable ambient air quality standards for ozone (1,2).
- 1.2 The more elaborate theoretical models generally require detailed organic species data obtained by multicomponent gas chromatography (3). The Empirical Kinetic Modeling Approach (EKMA), however, requires only the total non-methane organic compound (NMOC) concentration data; specifically, the average total NMOC concentration from 6 a.m. to 9 a.m. daily at the sampling location. The use of total NMOC concentration data in the EKMA substantially reduces the cost and complexity of the sampling and analysis system by not requiring qualitative and quantitative species identification.
- 1.3 Method T01, "Method for The Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS)", employs collection of certain volatile organic compounds on Tenax® GC with subsequent analysis by thermal desorption/cryogenic preconcentration and GC/MS identification. This method (T012) combines the same type of cryogenic concentration technique used in Method T01 for high sensitivity with the simple flame ionization detector (FID) of the GC for total NMOC measurements, without the GC columns and complex procedures necessary for species separation.

- 1.4 In a flame ionization detector, the sample is injected into a hydrogen-rich flame where the organic vapors burn producing ionized molecular fragments. The resulting ion fragments are then collected and detected. The FID is nearly a universal detector. However, the detector response varies with the species of [functional group in] the organic compound in an oxygen atmosphere. Because this method employs a helium or argon carrier gas, the detector response is nearly one for all compounds. Thus, the historical short-coming of the FID involving varying detector response to different organic functional groups is minimized.
- 1.5 The method can be used either for direct, in situ ambient measurements or (more commonly) for analysis of integrated samples collected in specially treated stainless steel canisters. EKMA models generally require 3-hour integrated NMOC measurements over the 6 a.m. to 9 a.m. period and are used by State or local agencies to prepare State Implementation Plans (SIPs) for ozone control to achieve compliance with the National Ambient Air Quality Standards (NAAQS) for ozone. For direct, in situ ambient measurements, the analyst must be present during the 6 a.m. to 9 a.m. period, and repeat measurements (approximately six per hour) must be taken to obtain the 6 a.m. to 9 a.m. average NMOC concentration. The use of sample canisters allows the collection of integrated air samples over the 6 a.m. to 9 a.m. period by unattended, automated samplers. This method has incorporated both sampling approaches.

2. Applicable Documents

2.1 ASTM Standards

- D1356 - Definition of Terms Related to Atmospheric Sampling and Analysis
- E260 - Recommended Practice for General Gas Chromatography Procedures
- E355 - Practice for Gas Chromatography Terms and Relationships

2.2 Other Documents

U. S. Environmental Protection Agency Technical Assistance Documents (4,5)

Laboratory and Ambient Air Studies (6-10)

3. Summary of Method

- 3.1 A whole air sample is either extracted directly from the ambient air and analyzed on site by the GC system or collected into a precleaned sample canister and analyzed off site.
- 3.2 The analysis requires drawing a fixed-volume portion of the sample air at a low flow rate through a glass-bead filled trap that is cooled to approximately -186°C with liquid argon. The cryogenic trap simultaneously collects and concentrates the NMOC (either via condensation or adsorption) while allowing the methane, nitrogen, oxygen, etc. to pass through the trap without retention. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and the analytical phases.
- 3.3 After the fixed-volume air sample has been drawn through the trap, a helium carrier gas flow is diverted to pass through the trap, in the opposite direction to the sample flow, and into an FID. When the residual air and methane have been flushed from the trap and the FID baseline restabilizes, the cryogen is removed and the temperature of the trap is raised to approximately 90°C .
- 3.4 The organic compounds previously collected in the trap revolatilize due to the increase in temperature and are carried into the FID, resulting in a response peak or peaks from the FID. The area of the peak or peaks is integrated, and the integrated value is translated to concentration units via a previously-obtained calibration curve relating integrated peak areas with known concentrations of propane.
- 3.5 By convention, concentrations of NMOC are reported in units of parts per million carbon (ppmC), which, for a specific compound, is the concentration by volume (ppmV) multiplied by the number of carbon atoms in the compound.

- 3.6 The cryogenic trap simultaneously concentrates the NMOC while separating and removing the methane from air samples. The technique is thus direct reading for NMOC and, because of the concentration step, is more sensitive than conventional continuous NMOC analyzers.

4. Significance

- 4.1 Accurate measurements of ambient concentrations of NMOC are important for the control of photochemical smog because these organic compounds are primary precursors of atmospheric ozone and other oxidants. Achieving and maintaining compliance with the NAAQS for ozone thus depends largely on control of ambient levels of NMOC.
- 4.2 The NMOC concentrations typically found at urban sites may range up to 5-7 ppmC or higher. In order to determine transport of precursors into an area, measurement of NMOC upwind of the area may be necessary. Upwind NMOC concentrations are likely to be less than a few tenths of 1 ppm.
- 4.3 Conventional methods that depend on gas chromatography and qualitative and quantitative species evaluation are excessively difficult and expensive to operate and maintain when speciated measurements are not needed. The method described here involves a simple, cryogenic preconcentration procedure with subsequent, direct, flame ionization detection. The method is sensitive and provides accurate measurements of ambient NMOC concentrations where speciated data are not required as applicable to the EKMA.

5. Definitions

[Note: Definitions used in this document and in any user-prepared Standard Operating Procedures (SOPs) should be consistent with ASTM Methods D1356 and E355. All abbreviations and symbols are defined within this document at point of use.]

T012-5

- 5.1 Absolute pressure - Pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as pounds-force per square inch absolute (psia).
- 5.2 Cryogen - A substance used to obtain very low trap temperatures in the NMOC analysis system. Typical cryogens are liquid argon (bp -185.7) and liquid oxygen (bp-183.0).
- 5.3 Dynamic calibration - Calibration of an analytical system with pollutant concentrations that are generated in a dynamic, flowing system, such as by quantitative, flow-rate dilution of a high concentration gas standard with zero gas.
- 5.4 EKMA - Empirical Kinetics Modeling Approach; an empirical model that attempts to relate morning ambient concentrations of non-methane organic compounds (NMOC) and NO_x with subsequent peak, downwind ambient ozone concentrations; used by pollution control agencies to estimate the degree of hydrocarbon emission reduction needed to achieve compliance with national ambient air quality standards for ozone.
- 5.5 Gauge pressure - Pressure measured with reference to atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure (0 psig) is equal to atmospheric pressure, or 14.7 psia (101 kPa).
- 5.6 In situ - In place; In situ measurements are obtained by direct, on-the-spot analysis, as opposed to subsequent, remote analysis of a collected sample.
- 5.7 Integrated sample - A sample obtained uniformly over a specified time period and representative of the average levels of pollutants during the time period.
- 5.8 NMOC - Nonmethane organic compounds; total organic compounds as measured by a flame ionization detector, excluding methane.
- 5.9 ppmC - Concentration unit of parts per million carbon; for a specific compound, ppmC is equivalent to parts per million by volume (ppmv) multiplied by the number of carbon atoms in the compound.
- 5.10 Sampling - The process of withdrawing or isolating a representative portion of an ambient atmosphere, with or without the simultaneous isolation of selected components for subsequent analysis.

6. Interferences

- 6.1 In field and laboratory evaluation, water was found to cause a positive shift in the FID baseline. The effect of this shift is minimized by carefully selecting the integration termination point and adjusted baseline used for calculating the area of the NMOC peak(s).
- 6.2 When using helium as a carrier gas, FID response is quite uniform for most hydrocarbon compounds, but the response can vary considerably for other types of organic compounds.

7. Apparatus

7.1 Direct Air Sampling (Figure 1)

- 7.1.1 Sample manifold or sample inlet line - to bring sample air into the analytical system.
- 7.1.2 Vacuum pump or blower - to draw sample air through a sample manifold or long inlet line to reduce inlet residence time. Maximum residence time should be no greater than 1 minute.

7.2 Remote Sample Collection in Pressurized Canisters (Figure 2)

- 7.2.1 Sample canister(s) - stainless steel, Summa®-polished vessel(s) or 4-6 L capacity (Scientific Instrumentation Specialists, Inc., P.O. Box 8941, Moscow, ID 83843), used for automatic collection of 3-hour integrated field air samples. Each canister should have a unique identification number stamped on its frame.
- 7.2.2 Sample pump - stainless steel, metal bellows type (Model MB-151, Metal Bellows Corp., 1075 Providence Highway, Sharon, MA 02067) capable of 2 atmospheres minimum output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.
- 7.2.3 Pressure gauge - 0-30 psig (0-240 kPa).
- 7.2.4 Solenoid valve - special electrically-operated, bistable solenoid valve (Skinner Magnetlatch Valve, New Britain,

CT), to control sample flow to the canister with negligible temperature rise (Figure 3). The use of the Skinner Magnelatch valve avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve, which would have to be energized during the entire sample period. This temperature rise in the valve could cause outgasing of organics from the Viton valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods or with a conventional mechanical timer and a special pulse circuit. Figure 3 [a] illustrates a simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer. However, with this simple circuit, the valve may operate unpredictably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 3[b].

- 7.2.5 Stainless steel orifice (or short capillary) - capable of maintaining a substantially constant flow over the sampling period (see Figure 4).
- 7.2.6 Particulate matter filter - 2 micron stainless steel sintered in-line type (see Figure 4).
- 7.2.7 Timer - used for unattended sample collection. Capable of controlling pump(s) and solenoid valve.

7.3 Sample Canister Cleaning (Figure 5)

- 7.3.1 Vacuum pump - capable of evacuating sample canister(s) to an absolute pressure of <5 mm Hg.
- 7.3.2 Manifold - stainless steel manifold with connections for simultaneously cleaning several canisters.
- 7.3.3 Shut off valve(s) - seven required.
- 7.3.4 Vacuum gauge - capable of measuring vacuum in the manifold to an absolute pressure of 5 mm Hg or less.

- 7.3.5 Cryogenic trap (2 required) - U-shaped open tubular trap cooled with liquid nitrogen or argon used to prevent contamination from back diffusion of oil from vacuum pump, and to provide clean, zero air to sample canister(s).
 - 7.3.6 Pressure gauge - 0-50 psig (0-345 kPa), to monitor zero air pressure.
 - 7.3.7 Flow control valve - to regulate flow of zero air into canister(s).
 - 7.3.8 Humidifier - water bubbler or other system capable of providing moisture to the zero air supply.
- 7.4 Analytical System (Figure 1)
- 7.4.1 FID detector system - including flow controls for the FID fuel and air, temperature control for the FID, and signal processing electronics. The FID burner air, hydrogen, and helium carrier flow rates should be set according to the manufacturer's instructions to obtain an adequate FID response while maintaining as stable a flame as possible through all phases of the analytical cycle.
 - 7.4.2 Chart recorder - capable of the output signal, to record FID response.
 - 7.4.3 Electronic integrator - capable of integrating the area of one or more FID response peaks and calculating peak area corrected for baseline drift. If a separate integrator and chart recorder are used, care must be exercised to be sure that these components do not interfere with each other electrically. Range selector controls on both the integrator and the FID analyzer may not provide accurate range ratios, so individual calibration curves should be prepared for each range to be used. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate baseline between the start and end of the integration period, and calculating the peak area.

Note: The FID (7.4.1), chart recorder (7.4.2), integrator (7.4.3), valve heater (7.4.5), and a trap heating system are conveniently provided by a standard laboratory chromatograph and associated integrator. EPA has adapted two such systems for the PDFID method: a Hewlett-Packard model 5880 (Hewlett-Packard Corp., Avondale, PA) and a Shimadzu model GC8APF (Shimadzu Scientific Instruments Inc., Columbia, MD; see Reference 5). Other similar systems may also be applicable.

- 7.4.4 Trap - the trap should be carefully constructed from a single piece of chromatographic-grade stainless steel tubing (0.32 cm O.D, 0.21 cm I.D.) as shown in Figure 6. The central portion of the trap (7-10 cm) is packed with 60/80 mesh glass beads, with small glass wool (dimethyldichlorosilane-treated) plugs to retain the beads. The trap must fit conveniently into the Dewar flask (7.4.9), and the arms must be of an appropriate length to allow the beaded portion of the trap to be submerged below the level of liquid cryogen in the Dewar. The trap should connect directly to the six-port valve, if possible, to minimize line length between the trap and the FID. The trap must be mounted to allow the Dewar to be slipped conveniently on and off the trap and also to facilitate heating of the trap (see 7.4.13).
- 7.4.5 Six-port chromatographic valve - Seiscor Model VIII (Seismograph Service Corp., Tulsa, OK), Valco Model 9110 (Valco Instruments Co., Houston, TX), or equivalent. The six-port valve and as much of the interconnecting tubing as practical should be located inside an oven or otherwise heated to 80 - 90°C to minimize wall losses or adsorption/desorption in the connecting tubing. All lines should be as short as practical.
- 7.4.6 Multistage pressure regulators - standard two-stage, stainless steel diaphragm regulators with pressure gauges, for helium, air, and hydrogen cylinders.
- 7.4.7 Pressure regulators - optional single stage, stainless steel, with pressure gauge, if needed, to maintain constant helium carrier and hydrogen flow rates.

- 7.4.8 Fine needle valve - to adjust sample flow rate through trap.
- 7.4.9 Dewar flask - to hold liquid cryogen to cool the trap, sized to contain submerged portion of trap.
- 7.4.10 Absolute pressure gauge - 0-450 mm Hg, (2 mm Hg scale divisions indicating units): to monitor repeatable volumes of sample air through cryogenic trap (Wallace and Tiernan, Model 61C-ID-0410, 25 Main Street, Belleville, NJ).
- 7.4.11 Vacuum reservoir - 1-2 L capacity, typically 1 L.
- 7.4.12 Gas purifiers - gas scrubbers containing Drierite® or silica gel and 5A molecular sieve to remove moisture and organic impurities in the helium, air, and hydrogen gas flows (Alltech Associates, Deerfield, IL). Note: Check purity of gas purifiers prior to use by passing zero-air through the unit and analyzing according to Section 11.4. Gas purifiers are clean if produce [contain] less than 0.02 ppmC hydrocarbons.
- 7.4.13 Trap heating system - chromatographic oven, hot water, or other means to heat the trap to 80° to 90°C. A simple heating source for the trap is a beaker or Dewar filled with water maintained at 80-90°C. More repeatable types of heat sources are recommended, including a temperature-programmed chromatograph oven, electrical heating of the trap itself, or any type of heater that brings the temperature of the trap up to 80-90°C in 1-2 minutes.
- 7.4.14 Toggle shut-off valves (2) - leak free, for vacuum valve and sample valve.
- 7.4.15 Vacuum pump - general purpose laboratory pump capable of evacuating the vacuum reservoir to an appropriate vacuum that allows the desired sample volume to be drawn through the trap.
- 7.4.16 Vent - to keep the trap at atmospheric pressure during trapping when using pressurized canisters.
- 7.4.17 Rotameter - to verify vent flow.

- 7.4.18 Fine needle valve (optional) - to adjust flow rate of sample from canister during analysis.
- 7.4.19 Chromatographic-grade stainless steel tubing (Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL, 60015, (312) 948-8600) and stainless steel plumbing fittings - for interconnections. All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.
- 7.5 Commercially Available PDFID System (5)
 - 7.5.1 A convenient and cost-effective modular PDFID system suitable for use with a conventional laboratory chromatograph is commercially available (NuTech Corporation, Model 8548, 2806 Cheek Road, Durham, NC, 27704, (919) 682-0402).
 - 7.5.2 This modular system contains almost all of the apparatus items needed to convert the chromatograph into a PDFID analytical system and has been designed to be readily available and easy to assemble.
- 8. Reagents and Materials
 - 8.1 Gas cylinders of helium and hydrogen - ultrahigh purity grade.
 - 8.2 Combustion air - cylinder containing less than 0.02 ppm hydrocarbons, or equivalent air source.
 - 8.3 Propane calibration standard - cylinder containing 1-100 ppm (3-300 ppmC) propane in air. The cylinder assay should be traceable to a National Bureau of Standards (NBS) Standard Reference Material (SRM) or to a NBS/EPA-approved Certified Reference Material (CRM).
 - 8.4 Zero air - cylinder containing less than 0.02 ppmC hydrocarbons. Zero air may be obtained from a cylinder of zero-grade compressed air scrubbed with Drierite® or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup

- of ambient air. All zero air should be passed through a liquid argon cold trap for final cleanup, then passed through a hydrocarbon-free water bubbler (or other device) for humidification.
- 8.5 Liquid cryogen - liquid argon (bp -185.7°C) or liquid oxygen, (bp -183°C) may be used as the cryogen. Experiments have shown no differences in trapping efficiency between liquid argon and liquid oxygen. However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195°C) should not be used because it causes condensation of oxygen and methane in the trap.

9. Direct Sampling

- 9.1 For direct ambient air sampling, the cryogenic trapping system draws the air sample directly from a pump-ventilated distribution manifold or sample line (see Figure 1). The connecting line should be of small diameter (1/8" O.D.) stainless steel tubing and as short as possible to minimize its dead volume.
- 9.2 Multiple analyses over the sampling period must be made to establish hourly or 3-hour NMOC concentration averages.

10. Sample Collection in Pressurized Canister(s)

For integrated pressurized canister sampling, ambient air is sampled by a metal bellows pump through a critical orifice (to maintain constant flow), and pressurized into a clean, evacuated, Summa®-polished sample canister. The critical orifice size is chosen so that the canister is pressurized to approximately one atmosphere above ambient pressure, at a constant flow rate over the desired sample period. Two canisters are connected in parallel for duplicate samples. The canister(s) are then returned to the laboratory for analysis, using the PDFID analytical system. Collection of ambient air samples in pressurized canisters provides the following advantages:

- o Convenient integration of ambient samples over a specific time period
- o Capability of remote sampling with subsequent central laboratory analysis
- o Ability to ship and store samples, if necessary

- o Unattended sample collection
- o Analysis of samples from multiple sites with one analytical system
- o Collection of replicate samples for assessment of measurement precision

With canister sampling, however, great care must be exercised in selecting, cleaning, and handling the sample canister(s) and sampling apparatus to avoid losses or contamination of the samples.

10.1 Canister Cleanup and Preparation

- 10.1.1 All canisters must be clean and free of any contaminants before sample collection.
- 10.1.2 Leak test all canisters by pressurizing them to approximately 30 psig [200 kPa (gauge)] with zero air. The use of the canister cleaning system (see Figure 5) may be adequate for this task. Measure the final pressure - close the canister valve, then check the pressure after 24 hours. If leak tight, the pressure should not vary more than ± 2 psig over the 24-hour period. Note leak check result on sampling data sheet, Figure 7.
- 10.1.3 Assemble a canister cleaning system, as illustrated in Figure 5. Add cryogen to both the vacuum pump and zero air supply traps. Connect the canister(s) to the manifold. Open the vent shut off valve and the canister valve(s) to release any remaining pressure in the canister. Now close the vent shut off valve and open the vacuum shut off valve. Start the vacuum pump and evacuate the canister(s) to ≤ 5.0 mm Hg (for at least one hour). [Note: On a daily basis or more often if necessary, blow-out the cryogenic traps with zero air to remove any trapped water from previous canister cleaning cycles.]
- 10.1.4 Close the vacuum and vacuum gauge shut off valves and open the zero air shut off valve to pressurize the canister(s) with moist zero air to approximately 30 psig [200 kPa (gauge)]. If a zero gas generator system is used,

the flow rate may need to be limited to maintain the zero air quality.

10.1.5 Close the zero shut off valve and allow canister(s) to vent down to atmospheric pressure through the vent shut off valve. Close the vent shut off valve. Repeat steps 10.1.3 through 10.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

10.1.6 As a "blank" check of the canister(s) and cleanup procedure, analyze the final zero-air fill of 100% of the canisters until the cleanup system and canisters are proven reliable. The check can then be reduced to a lower percentage of canisters. Any canister that does not test clean (compared to direct analysis of humidified zero air of less than 0.02 ppmC) should not be utilized.

10.1.7 The canister is then re-evacuated to ≤ 5.0 mm Hg, using the canister cleaning system, and remains in this condition until use. Close the canister valve, remove the canister from the canister cleaning system and cap canister connection with a stainless steel fitting. The canister is now ready for collection of an air sample. Attach an identification tag to the neck of each canister for field notes and chain-of-custody purposes.

10.2 Collection of Integrated Whole-Air Samples

10.2.1 Assemble the sampling apparatus as shown in Figure 2. The connecting lines between the sample pump and the canister(s) should be as short as possible to minimize their volume. A second canister is used when a duplicate sample is desired for quality assurance (QA) purposes (see Section 12.2.4). The small auxiliary vacuum pump purges the inlet manifold or lines with a flow of several L/min to minimize the sample residence time. The larger metal bellows pump takes a small portion of this sample to fill and pressurize the sample canister(s). Both pumps should be shock-mounted to minimize vibration. Prior to field use, each sampling system should be leak

tested. The outlet side of the metal bellows pump can be checked for leaks by attaching the 0-30 psig pressure gauge to the canister(s) inlet via connecting tubing and pressurizing to 2 atmospheres or approximately 29.4 psig. If pump and connecting lines are leak free pressure should remain at +2 psig for 15 minutes. To check the inlet side, plug the sample inlet and insure that there is no flow at the outlet of the pump.

- 10.2.2 Calculate the flow rate needed so that the canister(s) are pressurized to approximately one atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period, utilizing the following equation:

$$F = \frac{(P)(V)(N)}{(T)(60)}$$

where:

F = flow rate (cm³/min)

P = final canister pressure (atmospheres absolute)
= (P_g/P_a) + 1

V = volume of the canister (cm³)

N = number of canisters connected together for simultaneous sample collection

T = sample period (hours)

P_g = gauge pressure in canister, psig (kPa)

P_a = standard atmospheric pressure, 14.7 psig (101 kPa)

For example, if one 6-L canister is to be filled to 2 atmospheres absolute pressure (14.7 psig) in 3 hours, the flow rate would be calculated as follows:

$$F = \frac{2 \times 6000 \times 1}{3 \times 60} = 67 \text{ cm}^3/\text{min}$$

- 10.2.3 Select a critical orifice or hypodermic needle suitable to maintain a substantially constant flow at the calculated flow rate into the canister(s) over the desired sample period. A 30-gauge hypodermic needle, 2.5 cm

long, provides a flow of approximately 65 cm³/min with the Metal Bellows Model MBV-151 pump (see Figure 4). Such a needle will maintain approximately constant flow up to a canister pressure of about 10 psig (71 kPa), after which the flow drops with increasing pressure. At 14.7 psig (2 atmospheres absolute pressure), the flow is about 10% below the original flow.

- 10.2.4 Assemble the 2.0 micron stainless steel in-line particulate filter and position it in front of the critical orifice. A suggested filter-hypodermic needle assembly can be fabricated as illustrated in Figure 4.
- 10.2.5 Check the sampling system for contamination by filling two evacuated, cleaned canister(s) (See Section 10.1) with humidified zero air through the sampling system. Analyze the canisters according to Section 11.4. The sampling system is free of contamination if the canisters contain less than 0.02 ppmC hydrocarbons, similar to that of humidified zero air.
- 10.2.6 During the system contamination check procedure, check the critical orifice flow rate on the sampling system to insure that sample flow rate remains relatively constant ($\pm 10\%$) up to about 2 atmospheres absolute pressure (101 kPa). Note: A drop in the flow rate may occur near the end of the sampling period as the canister pressure approaches two atmospheres.
- 10.2.7 Reassemble the sampling system. If the inlet sample line is longer than 3 meters, install an auxiliary pump to ventilate the sample line, as illustrated in Figure 2.
- 10.2.8 Verify that the timer, pump(s) and solenoid valve are connected and operating properly.
- 10.2.9 Verify that the timer is correctly set for the desired sample period, and that the solenoid valve is closed.
- 10.2.10 Connect a cleaned, evacuated canister(s) (Section 10.1) to the non-contaminated sampling system, by way of the solenoid valve, for sample collection.

- 10.2.11 Make sure the solenoid valve is closed. Open the canister valve(s). Temporarily connect a small rotameter to the sample inlet to verify that there is no flow. Note: Flow detection would indicate a leaking (or open) solenoid valve. Remove the rotameter after leak detection procedure.
- 10.2.12 Fill out the necessary information on the Field Data Sheet (Figure 7).
- 10.2.13 Set the automatic timer to start and stop the pump or pumps to open and close the solenoid valve at the appropriate time for the intended sample period. Sampling will begin at the pre-determined time.
- 10.2.14 After the sample period, close the canister valve(s) and disconnect the canister(s) from the sampling system. Connect a pressure gauge to the canister(s) and briefly open and close the canister valve. Note the canister pressure on the Field Data Sheet (see Figure 7). The canister pressure should be approximately 2 atmospheres absolute [1 atmosphere or 101 kPa (gauge)]. Note: If the canister pressure is not approximately 2 atmospheres absolute (14.7 psig), determine and correct the cause before next sample. Re-cap canister valve.
- 10.2.15 Fill out the identification tag on the sample canister(s) and complete the Field Data Sheet as necessary. Note any activities or special conditions in the area (rain, smoke, etc.) that may affect the sample contents on the sampling data sheet.
- 10.2.16 Return the canister(s) to the analytical system for analysis.

11. Sample Analysis

11.1 Analytical System Leak Check

- 11.1.1 Before sample analysis, the analytical system is assembled (see Figure 1) and leak checked.

- 11.1.2 To leak check the analytical system, place the six-port gas valve in the trapping position. Disconnect and cap the absolute pressure gauge. Insert a pressure gauge capable of recording up to 60 psig at the vacuum valve outlet.
 - 11.1.3 Attach a valve and a zero air supply to the sample inlet port. Pressurize the system to about 50 psig (350 kPa) and close the valve.
 - 11.1.4 Wait approximately 3 hrs. and re-check pressure. If the pressure did not vary more than ± 2 psig, the system is considered leak tight.
 - 11.1.5 If the system is leak free, de-pressurize and reconnect absolute pressure gauge.
 - 11.1.6 The analytical system leak check procedure needs to be performed during the system checkout, during a series of analysis or if leaks are suspected. This should be part of the user-prepared SOP manual (see Section 12..
- 11.2 Sample Volume Determination
- 11.2.1 The vacuum reservoir and absolute pressure gauge are used to meter a precisely repeatable volume of sample air through the cryogenically-cooled trap, as follows: With the sample valve closed and the vacuum valve open, the reservoir is first evacuated with the vacuum pump to a predetermined pressure (e.g., 100 mm Hg). Then the vacuum valve is closed and the sample valve is opened to allow sample air to be drawn through the cryogenic trap and into the evacuated reservoir until a second predetermined reservoir pressure is reached (e.g., 300 mm Hg). The (fixed) volume of air thus sampled is determined by the pressure rise in the vacuum reservoir (difference between the predetermined pressures) as measured by the absolute pressure gauge (see Section 12.2.1).

11.2.2 The sample volume can be calculated by:

$$V_s = \frac{(\Delta P)(V_r)}{(P_s)}$$

where:

V_s = volume of air sampled (standard cm^3)

ΔP = pressure difference measured by gauge (mm Hg)

V_r = volume of vacuum reservoir (cm^3)
usually 1 L

P_s = standard pressure (760 mm Hg)

For example, with a vacuum reservoir of 1000 cm^3 and a pressure change of 200 mm Hg (100 to 300 mm Hg), the volume sampled would be 263 cm^3 . [Note: Typical sample volume using this procedure is between 200-300 cm^3 .]

11.2.3 The sample volume determination need only be performed once during the system check-out and shall be part of the user-prepared SOP Manual (see Section 12.1).

11.3 Analytical System Dynamic Calibration

11.3.1 Before sample analysis, a complete dynamic calibration of the analytical system should be carried out at five or more concentrations on each range to define the calibration curve. This should be carried out initially and periodically thereafter [may be done only once during a series of analyses]. This should be part of the user-prepared SOP Manual (See Section 12.1). The calibration should be verified with two or three-point calibration checks (including zero) each day the analytical system is used to analyze samples.

11.3.2 Concentration standards of propane are used to calibrate the analytical system. Propane calibration standards may be obtained directly from low concentration cylinder standards or by dilution of high concentration cylinder

standards with zero air (see Section 8.3). Dilution flow rates must be measured accurately, and the combined gas stream must be mixed thoroughly for successful calibration of the analyzer. Calibration standards should be sampled directly from a vented manifold or tee. Note: Remember that a propane NMOC concentration in ppmC is three times the volumetric concentration in ppm.

- 11.3.3 Select one or more combinations of the following parameters to provide the desired range or ranges (e.g., 0-1.0 ppmC or 0-5.0 ppmC): FID attenuator setting, output voltage setting, integrator resolution (if applicable), and sample volume. Each individual range should be calibrated separately and should have a separate calibration curve. Note: Modern GC integrators may provide automatic ranging such that several decades of concentration may be covered in a single range. The user-prepared SOP manual should address variations applicable to a specific system design (see Section 12.1).
- 11.3.4 Analyze each calibration standard three times according to the procedure in Section 11.4. Insure that flow rates, pressure gauge start and stop readings, initial cryogen liquid level in the line, timing, heating, integrator settings, and other variables are the same as those that will be used during analysis of ambient samples. Typical flow rates for the gases are: hydrogen, 30 cm³/minute; helium carrier, 30 cm³/minute; burner air, 400 cm³/minute.
- 11.3.5 Average the three analyses for each concentration standard and plot the calibration curve(s) as average integrated peak area reading versus concentration in ppmC. The relative standard deviation for the three analyses should be less

than 3% (except for zero concentration). Linearity should be expected; points that appear to deviate abnormally should be repeated. Response has been shown to be linear over a wide range (0-10,000 ppbC). If nonlinearity is observed, an effort should be made to identify and correct the problem. If the problem cannot be corrected, additional points in the nonlinear region may be needed to define the calibration curve adequately.

11.4 Analysis Procedure

- 11.4.1 Insure the analytical system has been assembled properly, leaked checked, and properly calibrated through a dynamic standard calibration. Light the FID detector and allow to stabilize.
- 11.4.2 Check and adjust the helium carrier pressure to provide the correct carrier flow rate for the system. Helium is used to purge residual air and methane from the trap at the end of the sampling phase and to carry the re-volatilized NMOC from the trap into the FID. A single-stage auxiliary regulator between the cylinder and the analyzer may not be necessary, but is recommended to regulate the helium pressure better than the multistage cylinder regulator. When an auxiliary regulator is used, the secondary stage of the two-stage regulator must be set at a pressure higher than the pressure setting of the single-stage regulator. Also check the FID hydrogen and burner air flow rates (see 11.3.4).
- 11.4.3 Close the sample valve and open the vacuum valve to evacuate the vacuum reservoir to a specific predetermined value (e.g., 100 mm Hg).
- 11.4.4 With the trap at room temperature, place the six-port valve in the inject position.
- 11.4.5 Open the sample valve and adjust the sample flow rate needle valve for an appropriate trap flow of 50-100 cm^3/min . Note: The flow will be lower later, when the trap is cold.

- 11.4.6 Check the sample canister pressure before attaching it to the analytical system and record on Field Data Sheet (see Figure 7). Connect the sample canister or direct sample inlet to the six-port valve, as shown in Figure 1. For a canister, either the canister valve or an optional fine needle valve installed between the canister and the vent is used to adjust the canister flow rate to a value slightly higher than the trap flow rate set by the sample flow rate needle valve. The excess flow exhausts through the vent, which assures that the sample air flowing through the trap is at atmospheric pressure. The vent is connected to a flow indicator such as a rotameter as an indication of vent flow to assist in adjusting the flow control valve. Open the canister valve and adjust the canister valve or the sample flow needle valve to obtain a moderate vent flow as indicated by the rotameter. The sample flow rate will be lower (and hence the vent flow rate will be higher) when the trap is cold.
- 11.4.7 Close the sample valve and open the vacuum valve (if it is already open) to evacuate the vacuum reservoir. Switch the six-port valve in the inject position and the vacuum valve open, open the sample valve for 2-3 minutes [with both valves open, the pressure reading won't change] to flush and condition the inlet lines.
- 11.4.8 Close the sample valve and evacuate the reservoir to the predetermined sample starting pressure (typically 100 mm Hg) as indicated by the absolute pressure gauge.
- 11.4.9 Switch the six-port valve to the sample position.
- 11.4.10 Submerge the trap in the cryogen. Allow a few minutes for the trap to cool completely (indicated when the cryogen stops boiling). Add cryogen to the initial level used during system dynamic calibration. The level of the cryogenic liquid should remain constant with respect to the trap and should completely cover the beaded portion of the trap.

- 11.4.11 Open the sample valve and observe the increasing pressure on the pressure gauge. When it reaches the specific pre-determined pressure (typically 300 mm Hg) representative of the desired sample volume (Section 11.2), close the sample valve.
- 11.4.12 Add a little cryogen or elevate the Dewar to raise the liquid level to a point slightly higher (3-15 mm) than the initial level at the beginning of the trapping.
Note: This insures that organics do not bleed from the trap and are counted as part of the NMOC peak(s).
- 11.4.13 Switch the 6-port valve to the inject position, keeping the cryogenic liquid on the trap until the methane and upset peaks have diminished (10-20 seconds). Now close the canister valve to conserve the remaining sample in the canister.
- 11.4.14 Start the integrator and remove the Dewar flask containing the cryogenic liquid from the trap.
- 11.4.15 Close the GC oven door and allow the GC oven (or alternate trap heating system) to heat the trap at a predetermined rate (typically, 30°C/min) to 90°. Heating the trap volatilizes the concentrated NMOC such that the FID produces integrated peaks. A uniform trap temperature rise rate (above 0°C) helps to reduce variability and facilitates more accurate correction for the moisture-shifted baseline. With a chromatograph oven to heat the trap, the following parameters have been found to be acceptable: initial temperature, 30°C; initial time, 0.20 minutes (following start of the integrator); heat rate, 30°/minute; final temperature, 90°C.
- 11.4.16 Use the same heating process and temperatures for both calibration and sample analysis. Heating the trap too quickly may cause an initial negative response that could hamper accurate integration. Some initial experimentation may be necessary to determine the optimal heating procedure for each system. Once established, the procedure should be consistent for each analysis as outlined in the user-prepared SOP Manual.

- 11.4.17 Continue the integration (generally, in the range of 1-2 minutes is adequate) only long enough to include all of the organic compound peaks and to establish the end point FID baseline, as illustrated in Figure 8. The integrator should be capable of marking the beginning and ending of peaks, constructing the appropriate operational baseline between the start and end of the integration period, and calculating the resulting corrected peak area. This ability is necessary because the moisture in the sample, which is also concentrated in the trap, will cause a slight positive baseline shift. This baseline shift starts as the trap warms and continues until all of the moisture is swept from the trap, at which time the baseline returns to its normal level. The shift always continues longer than the ambient organic peak(s). The integrator should be programmed to correct for this shifted baseline by ending the integration at a point after the last NMOC peak and prior to the return of the shifted baseline to normal (see Figure 8) so that the calculated operational baseline effectively compensates for the water-shifted baseline. Electronic integrators either do this automatically or they should be programmed to make this correction. Alternatively, analyses of humidified zero air prior to sample analyses should be performed to determine the water envelope and the proper blank value for correcting the ambient air concentration measurements accordingly. Heating and flushing of the trap should continue after the integration period has ended to insure all water has been removed to prevent buildup of water in the trap. Therefore, be sure that the 6-port valve remains in the inject position until all moisture has purged from the trap (3 minutes or longer).

- 11.4.18 Use the dynamic calibration curve (see Section 11.3) to convert the integrated peak area reading into concentration units (ppmC). Note that the NMOC peak shape may not be precisely reproducible due to variations in heating the trap, but the total NMOC peak area should be reproducible.
- 11.4.19 Analyze each canister sample at least twice and report the average NMOC concentration. Problems during an analysis occasionally will cause erratic or inconsistent results. If the first two analyses do not agree within $\pm 5\%$ relative standard deviation (RSD), additional analyses should be made to identify inaccurate measurements and produce a more accurate average (see also Section 12.2.).

12. Performance Criteria and Quality Assurance

This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

12.1 Standard Operating Procedures (SOPs)

- 12.1.1 Users should generate SOPs describing and documenting the following activities in their laboratory: (1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used; (2) preparation, storage, shipment, and handling of samples; (3) assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used; (4) canister storage and cleaning; and (5) all aspects of data recording and processing, including lists of computer hardware and software used.
- 12.1.2 SOPs should provide specific stepwise instructions and should be readily available to, and understood by, the laboratory personnel conducting the work.

12.2 Method Sensitivity, Accuracy, Precision and Linearity

12.2.1 The sensitivity and precision of the method is proportional to the sample volume. However, ice formation in the trap may reduce or stop the sample flow during trapping if the sample volume exceeds 10 cm³. Sample volumes below about 100-150 cm³ may cause increased measurement variability due to dead volume in lines and valves. For most typical ambient NMOC concentrations, sample volumes in the range of 200-400 cm³ appear to be appropriate. If a response peak obtained with a 400 cm³ sample is off scale or exceeds the calibration range, a second analysis can be carried out with a smaller volume. The actual sample volume need not be accurately known if it is precisely repeatable during both calibration and analysis. Similarly, the actual volume of the vacuum reservoir need not be accurately known. But the reservoir volume should be matched to the pressure range and resolution of the absolute pressure gauge so that the measurement of the pressure change in the reservoir, hence the sample volume, is repeatable within 1%. A 1000 cm³ vacuum reservoir and a pressure change of 200 mm Hg, measured with the specified pressure gauge, have provided a sampling precision of ± 1.31 cm³. A smaller volume reservoir may be used with a greater pressure change to accommodate absolute pressure gauges with lower resolution, and vice versa.

12.2.2 Some FID detector systems associated with laboratory chromatographs may have autoranging. Others may provide attenuator control and internal full-scale output voltage selectors. An appropriate combination should be chosen so that an adequate output level for accurate integration is obtained down to the detection limit; however, the electrometer or integrator must not be driven into saturation at the upper end of the calibration. Saturation of the electrometer may be indicated by flattening of the calibration curve at

high concentrations. Additional adjustments of range and sensitivity can be provided by adjusting the sample volume used, as discussed in Section 12.2.1.

- 12.2.3 System linearity has been documented (6) from 0 to 10,000 ppbC.
- 12.2.4 Some organic compounds contained in ambient air are "sticky" and may require repeated analyses before they fully appear in the FID output. Also, some adjustment may have to be made in the integrator off time setting to accommodate compounds that reach the FID late in the analysis cycle. Similarly, "sticky" compounds from ambient samples or from contaminated propane standards may temporarily contaminate the analytical system and can affect subsequent analyses. Such temporary contamination can usually be removed by repeated analyses of humidified zero air.
- 12.2.5 Simultaneous collection of duplicate samples decreases the possibility of lost measurement data from samples lost due to leakage or contamination in either of the canisters. Two (or more) canisters can be filled simultaneously by connecting them in parallel (see Figure 2(a)) and selecting an appropriate flow rate to accommodate the number of canisters (Section 10.2.2). Duplicate (or replicate) samples also allow assessment of measurement precision based on the differences between duplicate samples (or the standard deviations among replicate samples).

13. Method Modification

13.1 Sample Metering System

- 13.1.1 Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume during analysis is efficient and convenient, other techniques should work also.
- 13.1.2 A constant sample flow could be established with a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period.

A gas volume meter, such as a wet test meter, could also be used to measure the total volume of sample air drawn through the trap. These alternative techniques should be tested and evaluated as part of a user-prepared SOP manual.

13.2 FID Detector System

13.2.1 A variety of FID detector systems should be adaptable to the method.

13.2.2 The specific flow rates and necessary modifications for the helium carrier for any alternative FID instrument should be evaluated prior to use as part of the user-prepared SOP manual.

13.3 Range

13.3.1 It may be possible to increase the sensitivity of the method by increasing the sample volume. However, limitations may arise such as plugging of the trap by ice.

13.3.2 Any attempt to increase sensitivity should be evaluated as part of the user-prepared SOP manual.

13.4 Sub-Atmospheric Pressure Canister Sampling

13.4.1 Collection and analysis of canister air samples at sub-atmospheric pressure is also possible with minor modifications to the sampling and analytical procedures.

13.4.2 Method T0-14, "Integrated Canister Sampling for Selective Organics: Pressurized and Sub-atmospheric Collection Mechanism," addresses sub-atmospheric pressure canister sampling. Additional information can be found in the literature (11-17).

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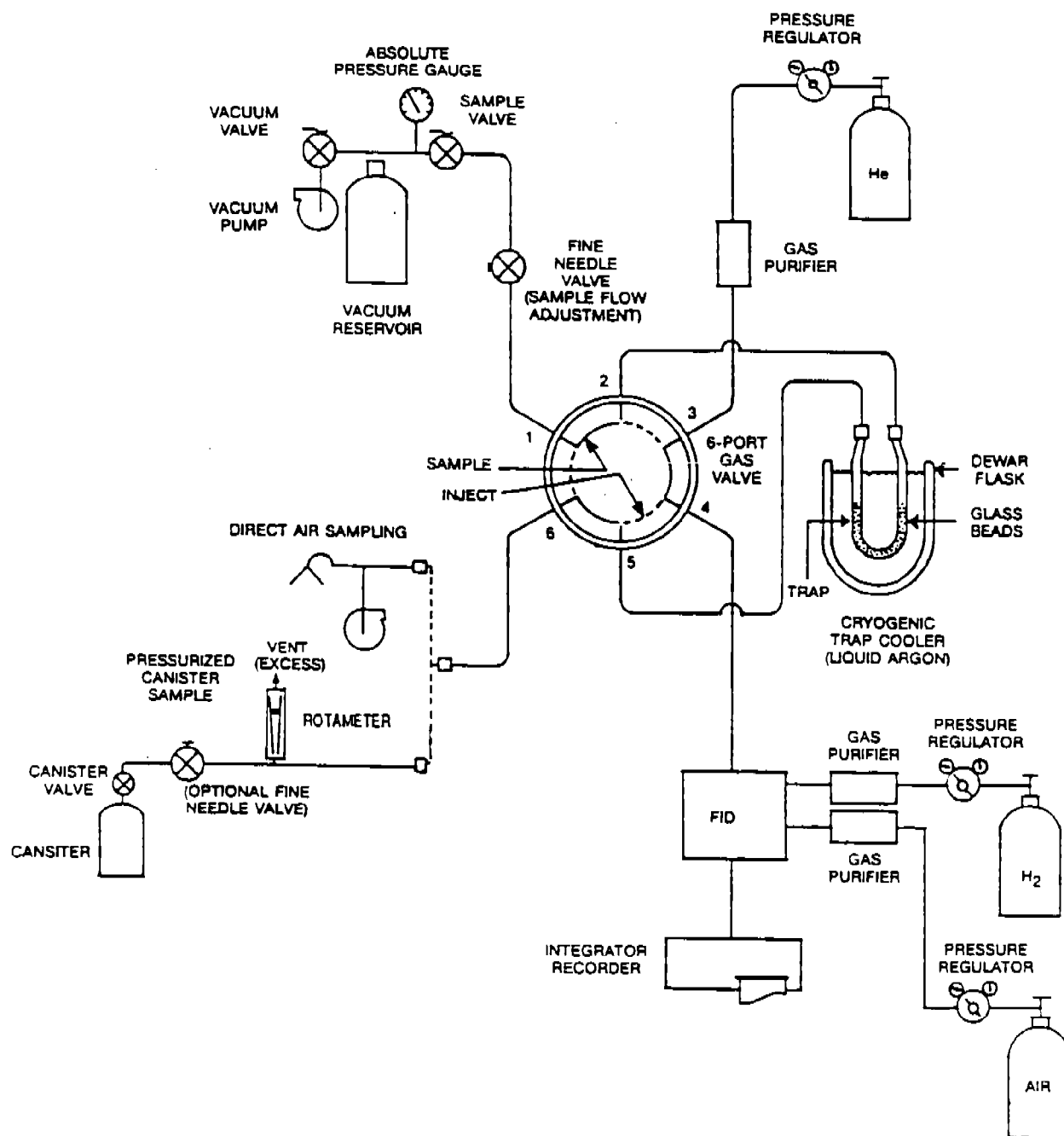


FIGURE 1. SCHEMATIC OF ANALYTICAL SYSTEM FOR NMOC—TWO SAMPLING MODES

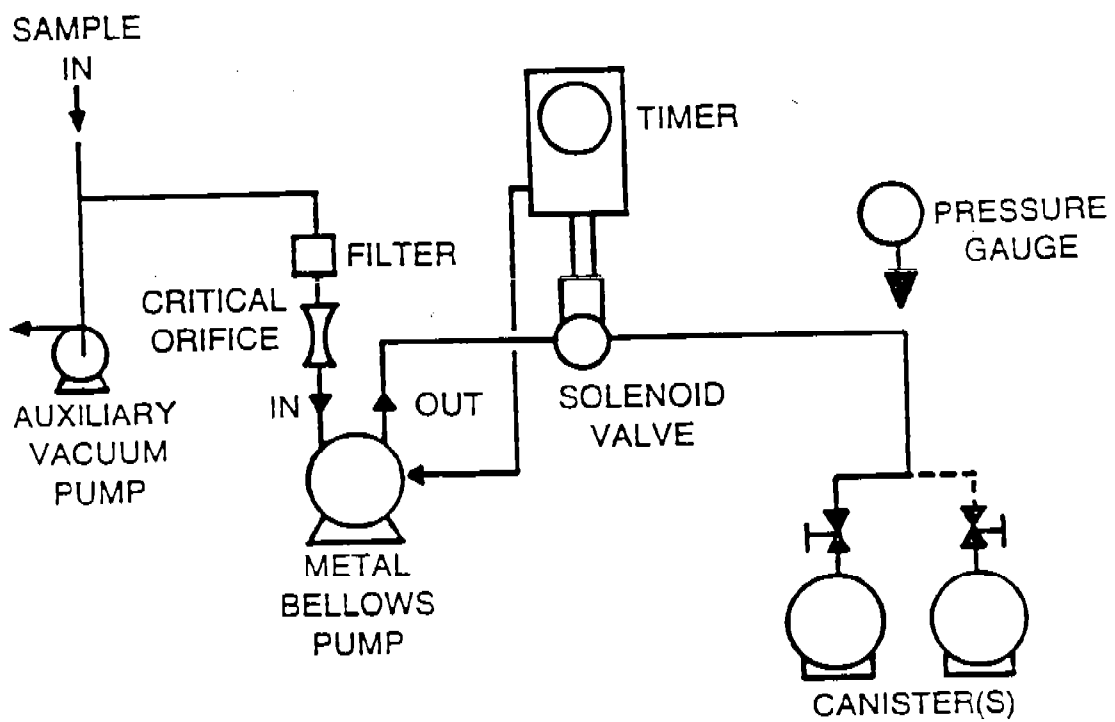


FIGURE 2. SAMPLE SYSTEM FOR AUTOMATIC COLLECTION OF 3-HOUR INTEGRATED AIR SAMPLES

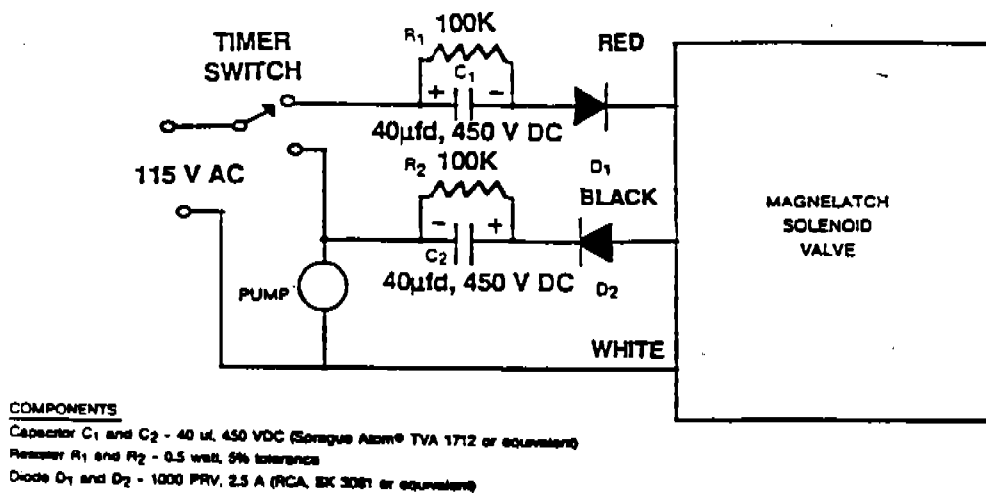


FIGURE 3[a]. SIMPLE CIRCUIT FOR OPERATING MAGNELATCH VALVE

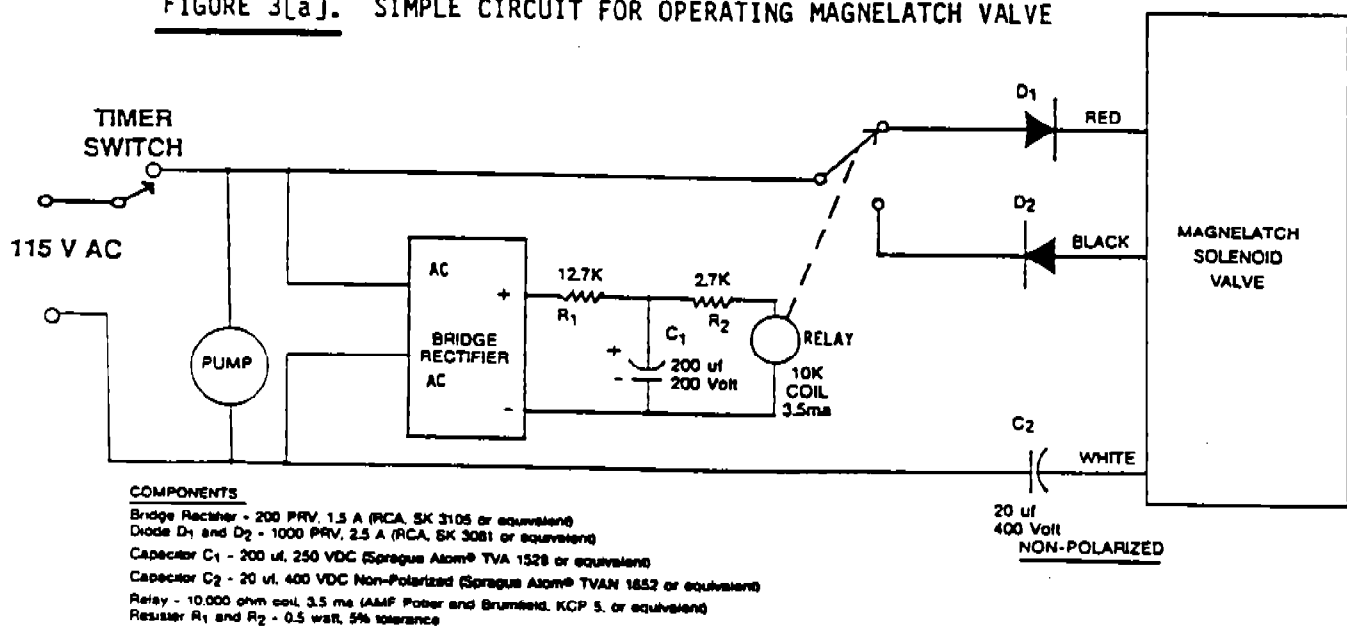


FIGURE 3[b]. IMPROVED CIRCUIT DESIGNED TO HANDLE POWER INTERRUPTIONS

FIGURE 3. ELECTRICAL PULSE CIRCUITS FOR DRIVING SKINNER MAGNELATCH SOLENOID VALVE WITH A MECHANICAL TIMER

T012-34

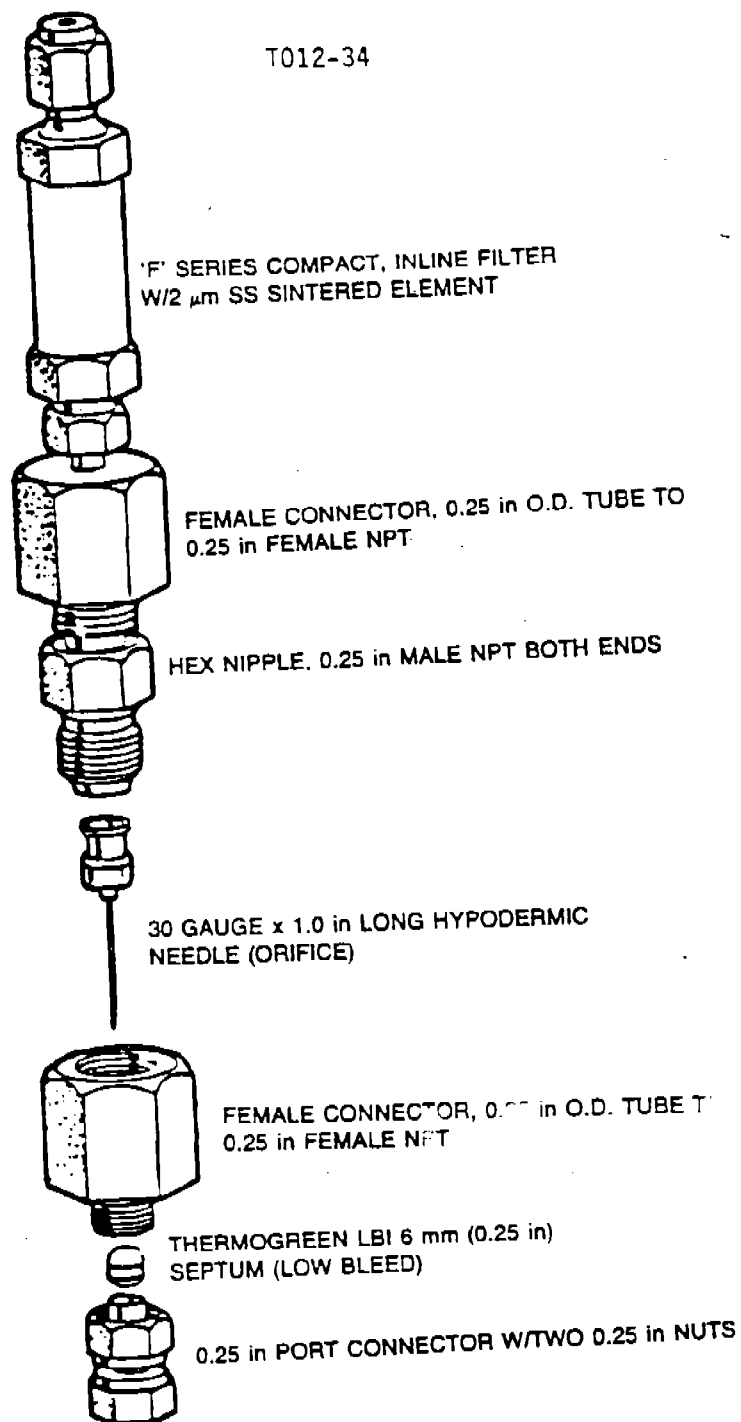
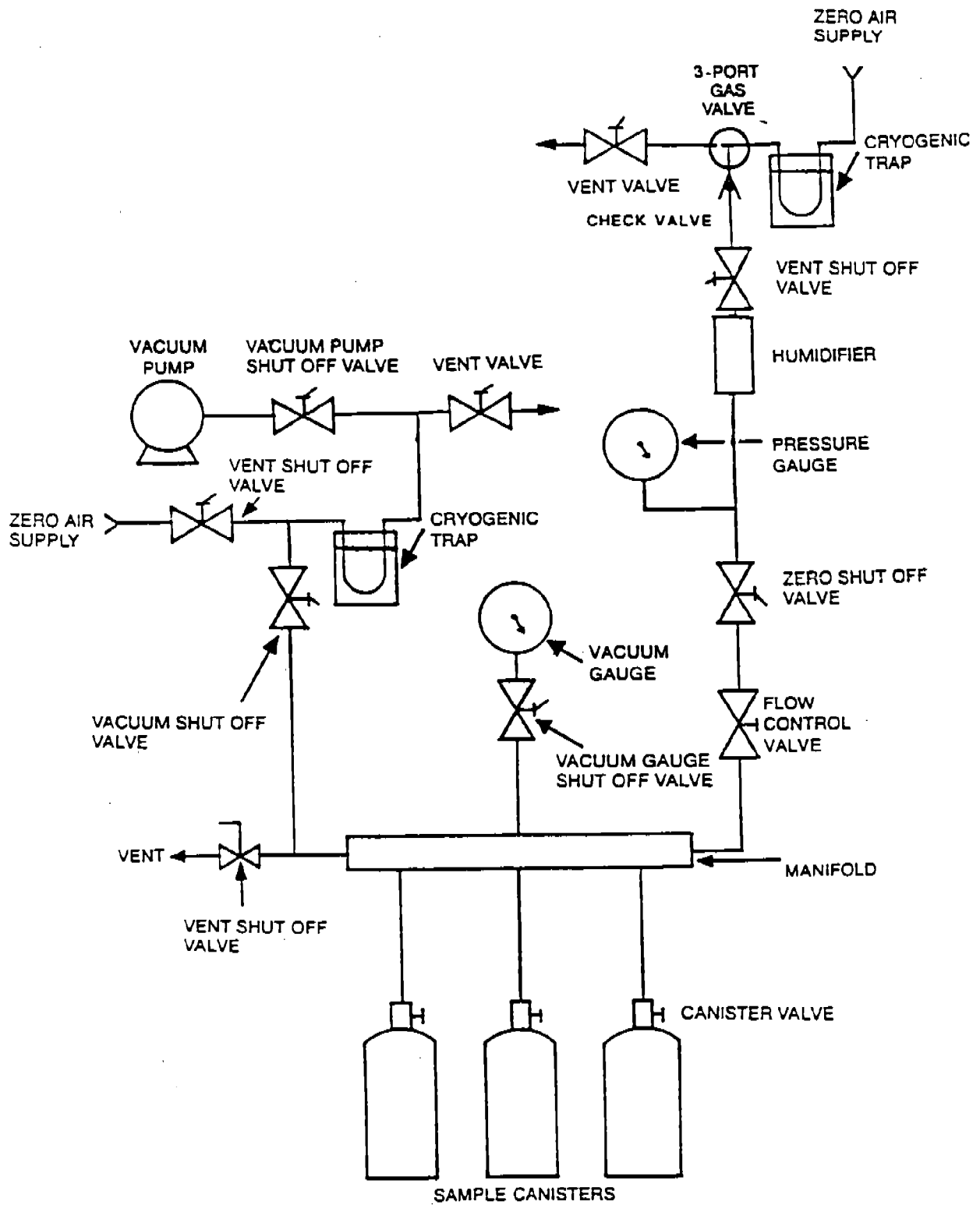


FIGURE 4. FILTER AND HYPODERMIC NEEDLE
ASSEMBLY FOR SAMPLE INLET FLOW
CONTROL

**FIGURE 5. CANISTER CLEANING SYSTEM**

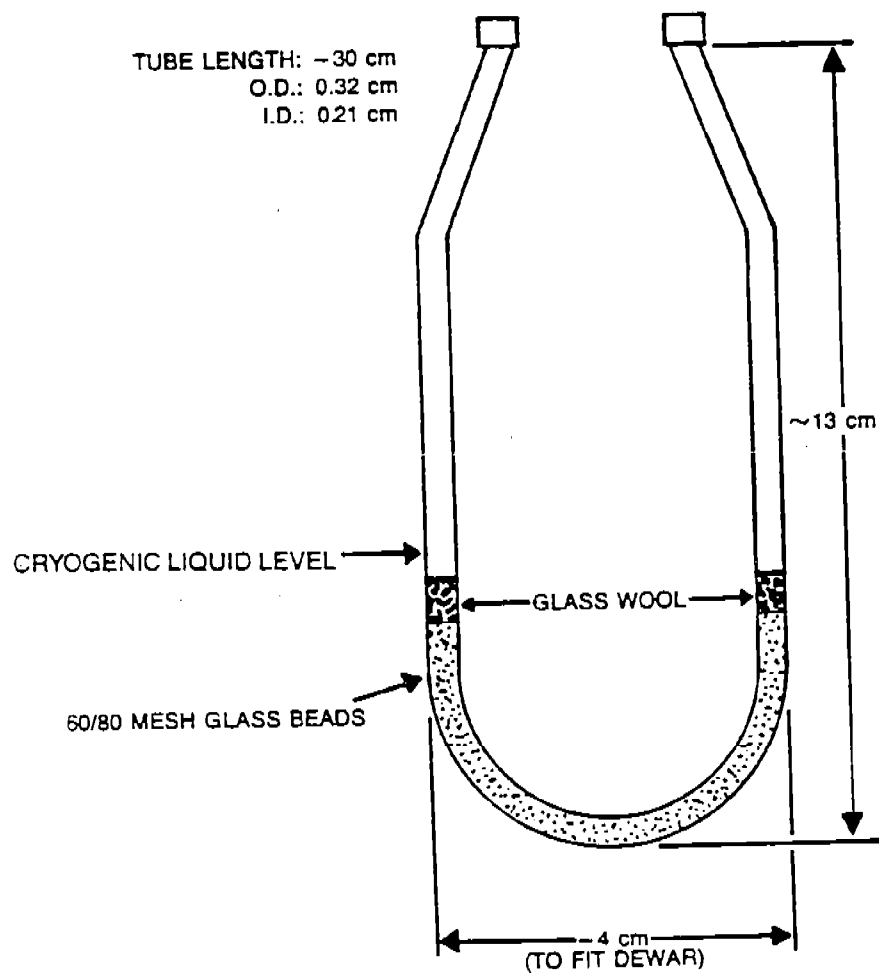


FIGURE 6. CRYOGENIC SAMPLE TRAP DIMENSIONS

GENERAL INFORMATION:

PROJECT: _____
SITE: _____
LOCATION: _____
MONITOR STATION NUMBER: _____
PUMP SERIAL NUMBER: _____

OPERATOR: _____
ORIFICE IDENTIFICATION: _____
FLOW RATE: _____
CALIBRATED BY: _____
LEAK CHECK _____ Pass _____ Fail _____

FIELD DATA:

[illegible]

_____ Date _____ Title _____ Signature _____

FIGURE 7. EXAMPLE SAMPLING DATA SHEET

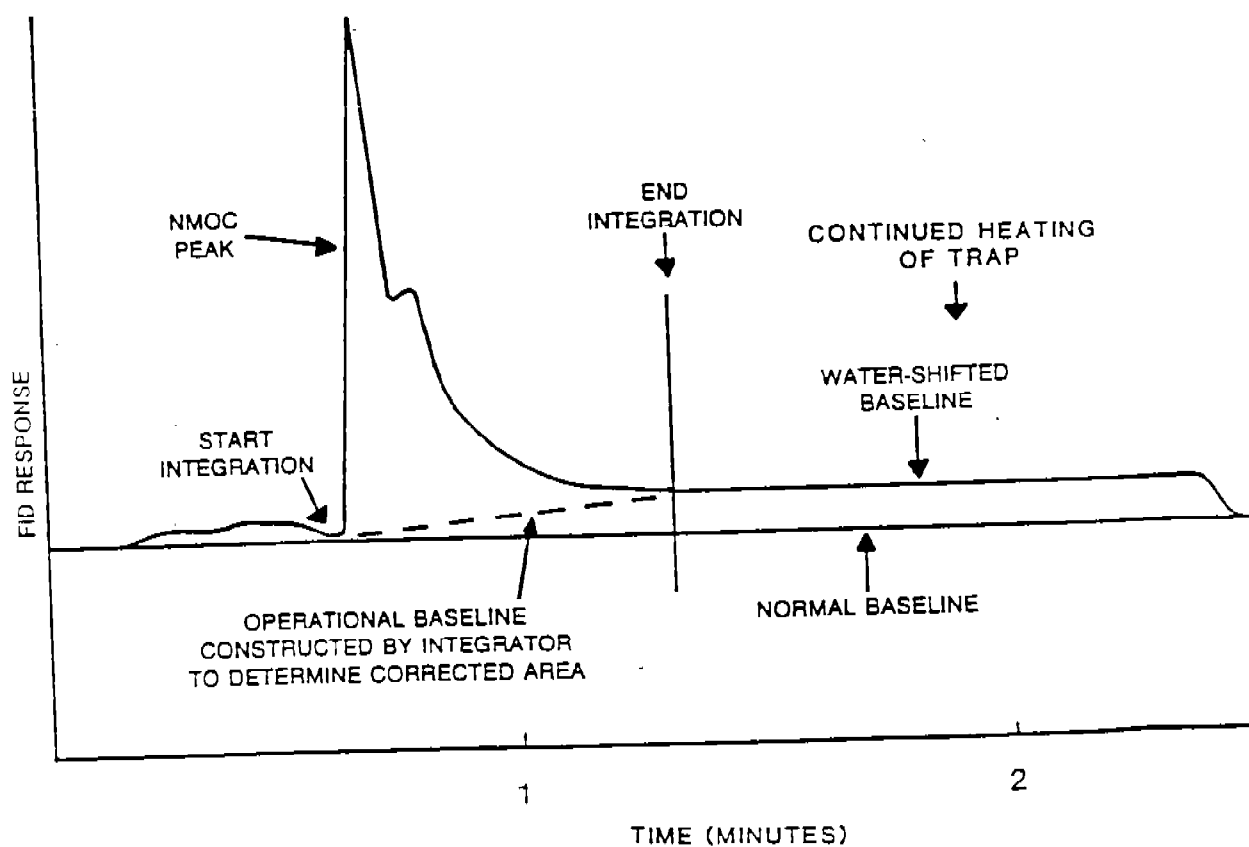


FIGURE 8. CONSTRUCTION OF OPERATIONAL BASELINE
AND CORRESPONDING CORRECTION OF
PEAK AREA

APPENDIX C

1990 NMOC MONITORING PROGRAM SITE DATA

APPENDIX C -- LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
C-1 Plot of NMOC concentration for Beaumont, TX	C-1
C-2 Plot of NMOC concentration for Baton Rouge, LA	C-4
C-3 Plot of NMOC concentration for Hartford, CT	C-8
C-4 Plot of NMOC concentration for Long Island, NY	C-11
C-5 Plot of NMOC concentration for Manhattan, NY	C-14
C-6 Plot of NMOC concentration for Newark, NJ	C-18
C-7 Plot of NMOC concentration for Plainfield, NJ	C-21

APPENDIX C -- LIST OF TABLES

<u>Table</u>	<u>Page</u>
C-1 SUMMARY OF THE 1989 NMOC DATA FOR BEAUMONT, TX (BMTX)	C-2
C-2 SUMMARY OF THE 1989 NMOC DATA FOR BATON ROUGE, LA (BRLA)	C-6
C-3 SUMMARY OF THE 1989 NMOC DATA FOR HARTFORD, CT (HTCT)	C-9
C-4 SUMMARY OF THE 1989 NMOC DATA FOR LONG ISLAND, NY (LINY)	C-12
C-5 SUMMARY OF THE 1989 NMOC DATA FOR MANHATTAN, NY (MNY)	C-16
C-6 SUMMARY OF THE 1989 NMOC DATA FOR NEWARK, NJ (NWNJ)	C-19
C-7 SUMMARY OF THE 1989 NMOC DATA FOR PLAINFIELD, NJ (PLNJ)	C-22

1

2

3

Beaumont, TX

1990 NMOC Program - BMTX

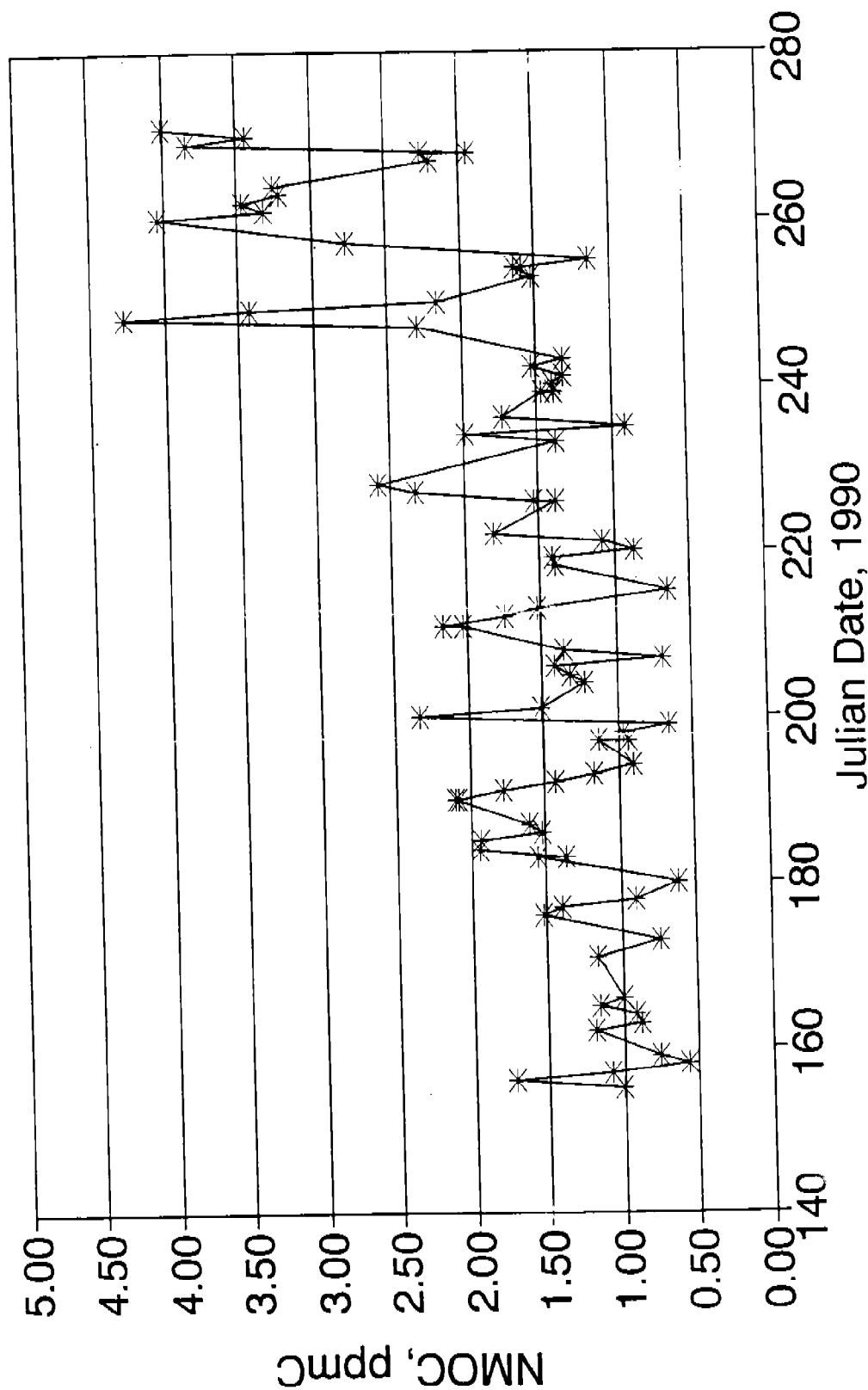


Figure C-1 . Plot of NMOC concentration for Beaumont, TX .

TABLE C-1. SUMMARY OF THE 1990 NMOC DATA FOR BEAUMONT, TX (BMTX)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
04-Jun-90	155	1006	659	11.8	13.0	C	1.002	
05-Jun-90	156	1005	838	11.2	11.0	D	1.719	
06-Jun-90	157	1012	772	11.5	13.0	B	1.083	
07-Jun-90	158	1023	690	11.5	11.0	B	0.558	
08-Jun-90	159	1024	766	11.2	12.0	A	0.754	
11-Jun-90	162	1033	783	11.5	13.0	C	1.187	
12-Jun-90	163	1039	676	11.5	13.0	D	0.883	
13-Jun-90	164	1056	146	11.5	12.0	B	0.908	
14-Jun-90	165	1051	400	11.5	12.0	C	1.150	
15-Jun-90	166	1057	685	12.0	14.3	A	0.999	
20-Jun-90	171	1086	853	11.0	12.0	D	1.165	1.166
22-Jun-90	173	1100	48	10.8	9.0	D	0.739	
25-Jun-90	176	1105	878	11.2	12.0	C	1.520	
26-Jun-90	177	1114	658	11.5	12.0	D	1.396	1.236
27-Jun-90	178	1115	928	11.5	12.0	B	0.895	0.868
29-Jun-90	180	1135	657	11.5	13.0	A	0.613	
02-Jul-90	183	1141	630	13.0	14.0	C	1.550	1.323
02-Jul-90	183	1140	632	13.0	16.0	C	1.367	
03-Jul-90	184	1150	74	22.5	24.0	B	1.938	
04-Jul-90	185	1153	885	11.1	12.0	C	1.930	
05-Jul-90	186	1155	656	12.0	12.0	C	1.520	
06-Jul-90	187	1173	649	12.1	12.0	A	1.610	
09-Jul-90	190	1171	838	13.0	16.0	A	2.100	
09-Jul-90	190	1163	897	13.0	16.0	A	2.079	
10-Jul-90	191	1181	149	11.5	12.0	A	1.770	
11-Jul-90	192	1192	618	11.5	12.0	D	1.423	
12-Jul-90	193	1199	666	11.5	14.0	D	1.160	
13-Jul-90	194	1202	77	11.0	14.0	D	0.901	0.963
16-Jul-90	197	1215	648	14.0	13.0	B	1.130	
16-Jul-90	197	1214	193	16.0	13.0	A	0.936	
17-Jul-90	198	1222	60	12.0	12.0	D	0.961	
18-Jul-90	199	1235	762	14.0	14.0	C	0.662	
19-Jul-90	200	1243	800	11.5	13.0	C	2.335	
20-Jul-90	201	1256	690	11.0	13.0	C	1.514	
23-Jul-90	204	1262	860	11.5	12.0	C	1.220	
24-Jul-90	205	1269	131	11.0	12.0	D	1.310	
25-Jul-90	206	1280	853	11.0	12.0	C	1.415	
26-Jul-90	207	1284	663	11.5	12.0	D	0.691	
27-Jul-90	208	1299	36	11.0	12.0	C	1.349	
30-Jul-90	211	1302	60	13.0	14.0	C	2.030	
30-Jul-90	211	1301	717	13.0	14.0	D	2.166	
31-Jul-90	212	1320	630	11.5	14.0	C	1.737	
01-Aug-90	213	1321	766	11.5	12.0	D	1.523	1.59
03-Aug-90	215	1332	649	20.0	22.0	C	0.647	0.669
06-Aug-90	218	1337	634	11.5	13.0	D	1.390	
07-Aug-90	219	1345	854	8.0	9.0	D	1.415	
08-Aug-90	220	1356	651	11.5	12.0	D	0.871	0.989
09-Aug-90	221	1360	765	10.0	10.0	D	1.079	
10-Aug-90	222	1646	783	9.5	10.0	C	1.810	
14-Aug-90	226	1388	711	11.0	11.0	A	1.386	
14-Aug-90	226	1389	626	11.0	11.0	B	1.528	
15-Aug-90	227	1401	400	7.5	8.0	C	2.330	
16-Aug-90	228	1402	875	7.5	8.0	D	2.580	
21-Aug-90	233	1422	776	17.0	18.0	D	1.372	

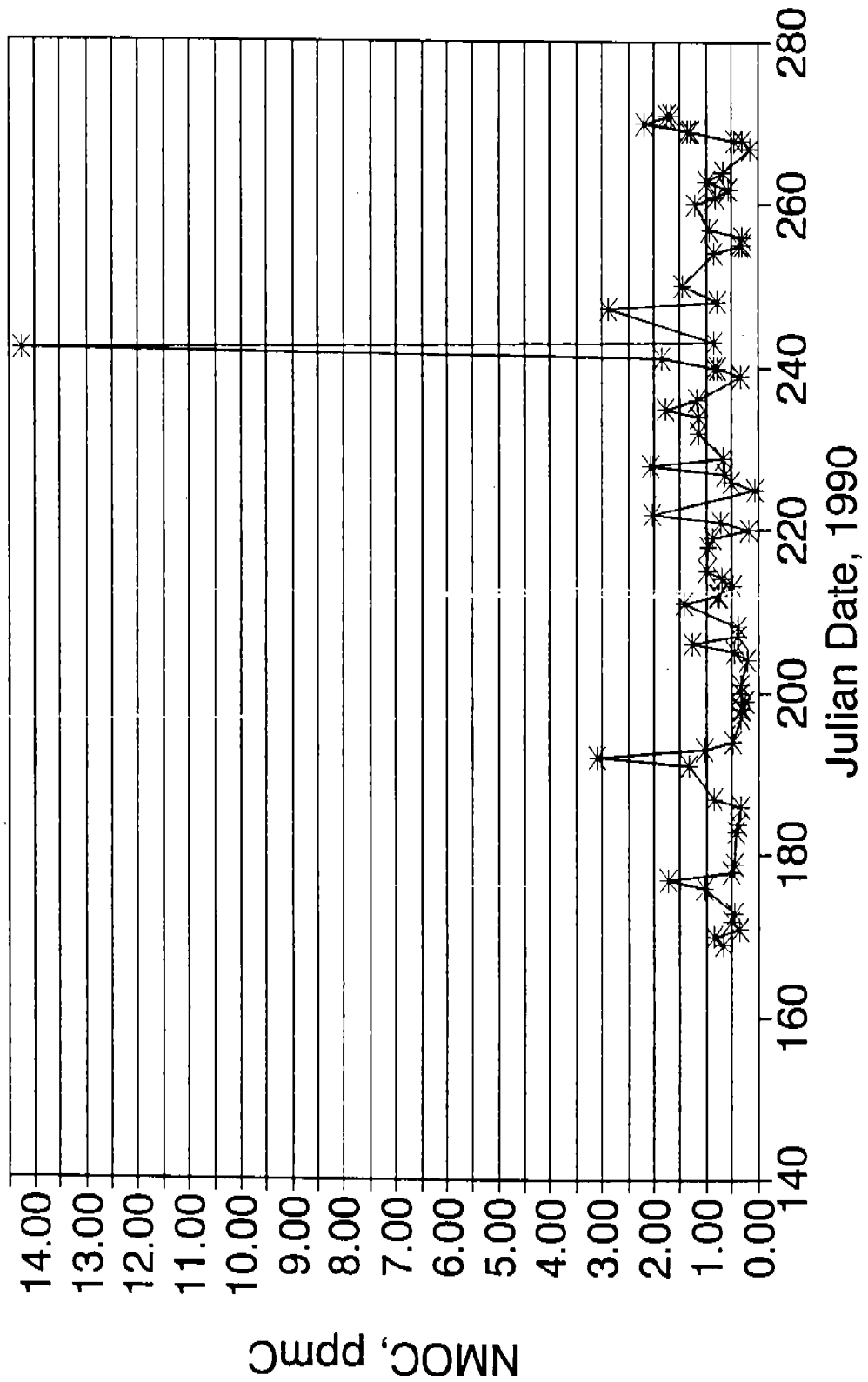
TABLE C-1. SUMMARY OF THE 1990 NMOC DATA FOR BEAUMONT, TX (BMTX)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
22-Aug-90	234	1431	91	16.5	17.0	C	1.981	
23-Aug-90	235	1440	131	13.0	19.0	B	0.909	
24-Aug-90	236	1448	676	13.5	18.0	A	1.737	
27-Aug-90	239	1453	607	18.0	19.5	D	1.469	
27-Aug-90	239	1452	872	18.0	19.0	C	1.386	
28-Aug-90	240	1455	137	16.0	18.0	C	1.391	
29-Aug-90	241	1472	684	17.5	18.0	B	1.320	
30-Aug-90	242	1476	400	16.0	18.0	D	1.532	
31-Aug-90	243	1475	113	16.0	17.0	D	1.326	
04-Sep-90	247	1493	776	18.0	18.0	B	2.299	
05-Sep-90	248	1502	618	17.5	18.0	D	4.283	
06-Sep-90	249	1509	870	16.0	17.0	A	3.423	
07-Sep-90	250	1513	780	17.5	18.0	A	2.161	
10-Sep-90	253	1525	80	16.0	18.0	C	1.523	
11-Sep-90	254	1534	306	16.0	18.0	C	1.633	
11-Sep-90	254	1535	685	16.0	18.0	D	1.588	
12-Sep-90	255	1538	885	16.0	18.0	D	1.145	
14-Sep-90	257	1550	151	16.0	17.0	D	2.777	
17-Sep-90	260	1559	833	16.0	17.0	C	4.040	
18-Sep-90	261	1573	191	16.0	17.0	B	3.323	
19-Sep-90	262	1588	868	16.0	17.0	C	3.466	
20-Sep-90	263	1587	164	16.0	16.0	D	3.220	
21-Sep-90	264	1596	854	16.0	16.0	D	3.260	3.238
24-Sep-90	267	1598	624	21.0	17.0	D	2.195	
25-Sep-90	268	1611	111	14.0	15.0	D	2.258	
25-Sep-90	268	1610	176	14.0	15.0	A	1.946	
26-Sep-90	269	1609	813	17.0	18.0	D	3.836	
27-Sep-90	270	1615	833	16.0	17.0	A	3.435	
28-Sep-90	271	1626	178	16.0	16.0	C	4.008	

Baton Rouge, LA

1990 NMOC Program - BRLA (Expanded)



Baton Rouge, LA

1990 NMOC Program - BRLA

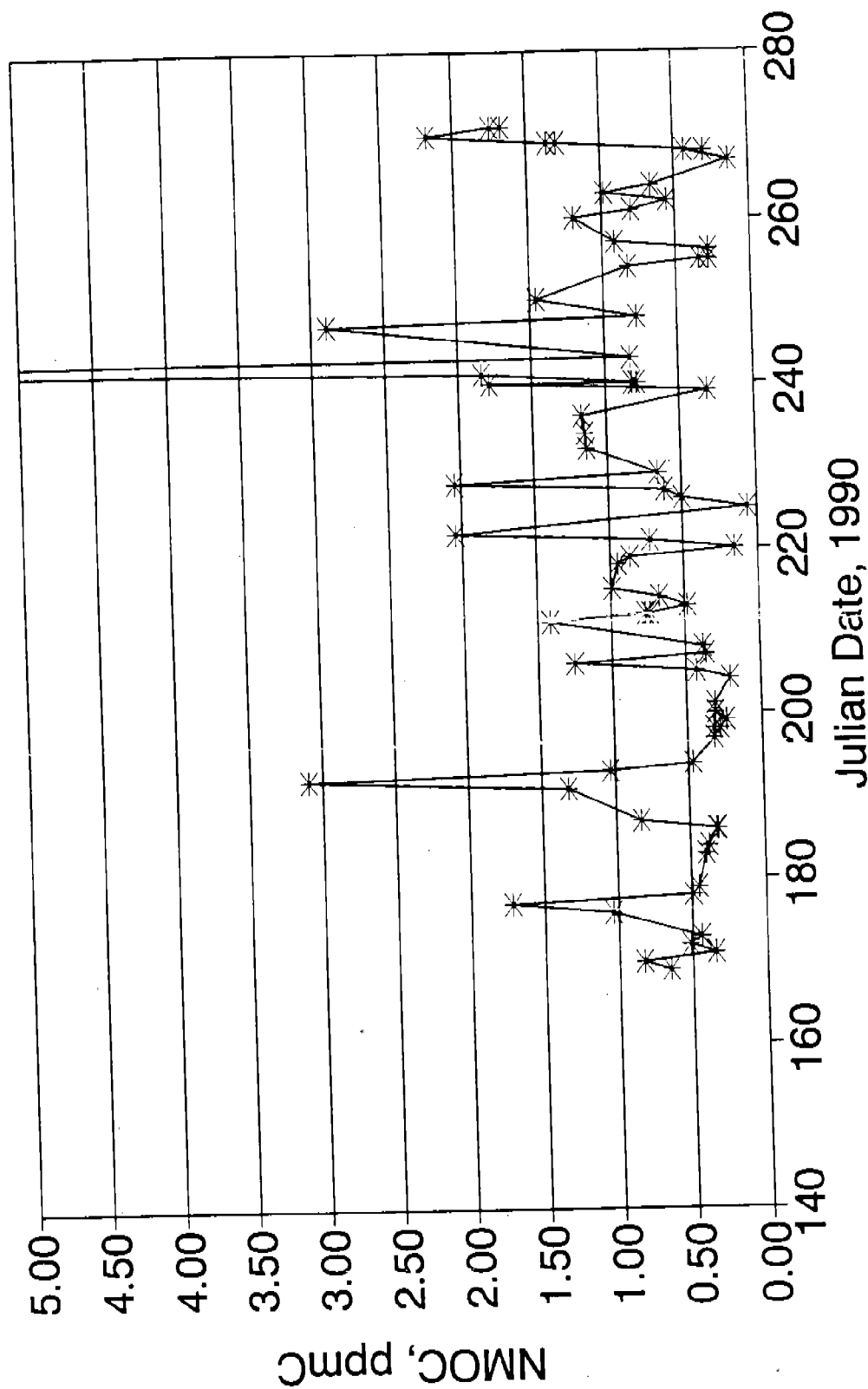


Figure C-2. Plot of NMOC concentration for Baton Rouge, LA.

TABLE C-2. SUMMARY OF THE 1990 NMOC DATA FOR BATON ROUGE, LA (BRLA)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
18-Jun-90	169	1069	762	14.0	12.5	D	0.651	
19-Jun-90	170	1064	20	13.0	12.0	D	0.838	
20-Jun-90	171	1078	17	13.0	12.0	D	0.346	0.213
21-Jun-90	172	1089	796	14.0	13.0	A	0.515	
22-Jun-90	173	1094	775	14.0	13.0	D	0.444	
25-Jun-90	176	1103	667	14.5	13.0	C	1.030	
26-Jun-90	177	1111	607	14.0	13.0	C	1.713	1.767
27-Jun-90	178	1110	666	15.0	12.0	D	0.495	
28-Jun-90	179	1127	854	13.0	15.0	C	0.456	
02-Jul-90	183	1149	678	14.0	13.0	D	0.398	0.441
03-Jul-90	184	1148	775	14.0	13.0	C	0.382	
05-Jul-90	186	1160	104	15.0	15.0	C	0.313	
05-Jul-90	186	1159	20	17.0	15.0	C	0.320	
06-Jul-90	187	1174	780	15.0	15.0	B	0.838	
10-Jul-90	191	1184	860	14.0	12.0	A	1.320	
11-Jul-90	192	1197	676	15.0	14.0	C	3.099	
12-Jul-90	193	1198	711	14.0	13.0	C	1.031	
13-Jul-90	194	1203	197	14.0	12.0	C	0.474	0.506
16-Jul-90	197	1218	651	15.0	14.0	B	0.319	0.867
17-Jul-90	198	1224	833	17.0	15.0	D	0.279	0.313
17-Jul-90	198	1223	137	15.0	12.0	C	0.327	
18-Jul-90	199	1230	780	15.0	14.0	D	0.243	0.285
19-Jul-90	200	1241	18	12.0	10.0	C	0.315	
20-Jul-90	201	1244	681	15.0	13.0	D	0.318	
23-Jul-90	204	1255	675	14.0	14.0	D	0.207	0.275
24-Jul-90	205	1267	92	14.0	13.0	D	0.432	0.479
25-Jul-90	206	1274	48	13.0	14.0	A	1.262	
26-Jul-90	207	1277	874	14.0	15.0	C	0.367	0.402
27-Jul-90	208	1283	719	15.0	16.0	D	0.383	
30-Jul-90	211	1300	77	15.0	16.0	D	1.416	
31-Jul-90	212	1310	762	17.0	16.0	A	0.740	
31-Jul-90	212	1309	897	17.0	16.0	B	0.766	
01-Aug-90	213	1322	628	15.0	13.0	D	0.487	
02-Aug-90	214	1327	838	14.0	14.0	B	0.679	
03-Aug-90	215	1333	707	15.0	14.0	D	0.989	
06-Aug-90	218	1351	692	15.0	15.0	C	0.954	
07-Aug-90	219	1352	792	15.0	16.0	D	0.860	
08-Aug-90	220	1355	777	30.0	30.0	C	0.154	
09-Aug-90	221	1363	193	14.0	15.0	C	0.723	
10-Aug-90	222	1384	789	15.0	14.0	B	2.040	2.147
13-Aug-90	225	1374	630	36.0	32.0	D	0.055	
14-Aug-90	226	1387	80	30.0	30.0	D	0.504	
14-Aug-90	226	1386	833	30.0	30.0	C	0.507	0.537
15-Aug-90	227	1395	52	14.0	15.0	D	0.618	
16-Aug-90	228	1406	658	14.0	15.0	D	2.046	
17-Aug-90	229	1405	674	14.0	13.0	C	0.663	
20-Aug-90	232	1416	149	14.0	16.0	D	1.140	
22-Aug-90	234	1430	671	14.0	14.0	D	1.156	
23-Aug-90	235	1433	656	14.0	14.0	D	1.785	
24-Aug-90	236	1437	793	30.0	30.0	B	1.172	
27-Aug-90	239	1441	789	15.0	15.0	A	0.318	
28-Aug-90	240	1467	626	18.0	18.0	B	0.789	
28-Aug-90	240	1466	624	18.0	18.0	A	0.826	
29-Aug-90	241	1469	37	14.0	14.0	A	1.844	

TABLE C-2 SUMMARY OF THE 1990 NMOC DATA FOR BATON ROUGE, LA (BRIA)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
30-Aug-90	242	1478	823	14.0	14.0	C	14.255	14.912
31-Aug-90	243	1488	766	14.0	13.0	B	0.832	
04-Sep-90	247	1492	659	15.0	15.0	A	2.890	0.78
05-Sep-90	248	1500	874	14.0	14.0	D	0.778	
07-Sep-90	250	1519	131	13.0	13.0	D	1.455	
11-Sep-90	254	1533	400	14.0	14.0	A	0.836	
12-Sep-90	255	1544	813	17.0	17.0	B	0.277	
12-Sep-90	255	1543	928	17.0	17.0	A	0.342	
13-Sep-90	256	1554	607	14.0	14.0	D	0.281	
14-Sep-90	257	1560	776	18.0	14.0	D	0.920	
17-Sep-90	260	1565	842	14.0	13.0	D	1.191	
18-Sep-90	261	1577	137	13.0	14.0	C	0.801	
19-Sep-90	262	1583	828	14.0	12.0	D	0.562	
20-Sep-90	263	1590	162	14.0	13.0	D	0.983	
21-Sep-90	264	1597	50	14.0	13.0	C	0.666	
24-Sep-90	267	1605	60	14.0	14.0	C	0.130	
25-Sep-90	268	1616	762	18.0	18.0	B	0.299	
25-Sep-90	268	1613	618	17.0	18.0	C	0.434	
26-Sep-90	269	1621	137	17.0	18.0	C	1.363	
26-Sep-90	269	1620	17	17.0	18.0	D	1.296	
27-Sep-90	270	1627	409	14.0	16.0	D	2.185	
28-Sep-90	271	1632	697	17.0	17.0	B	1.669	
28-Sep-90	271	1631	30	17.0	17.0	A	1.744	

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Hartford, CT

1990 NMOC Program - HTCT

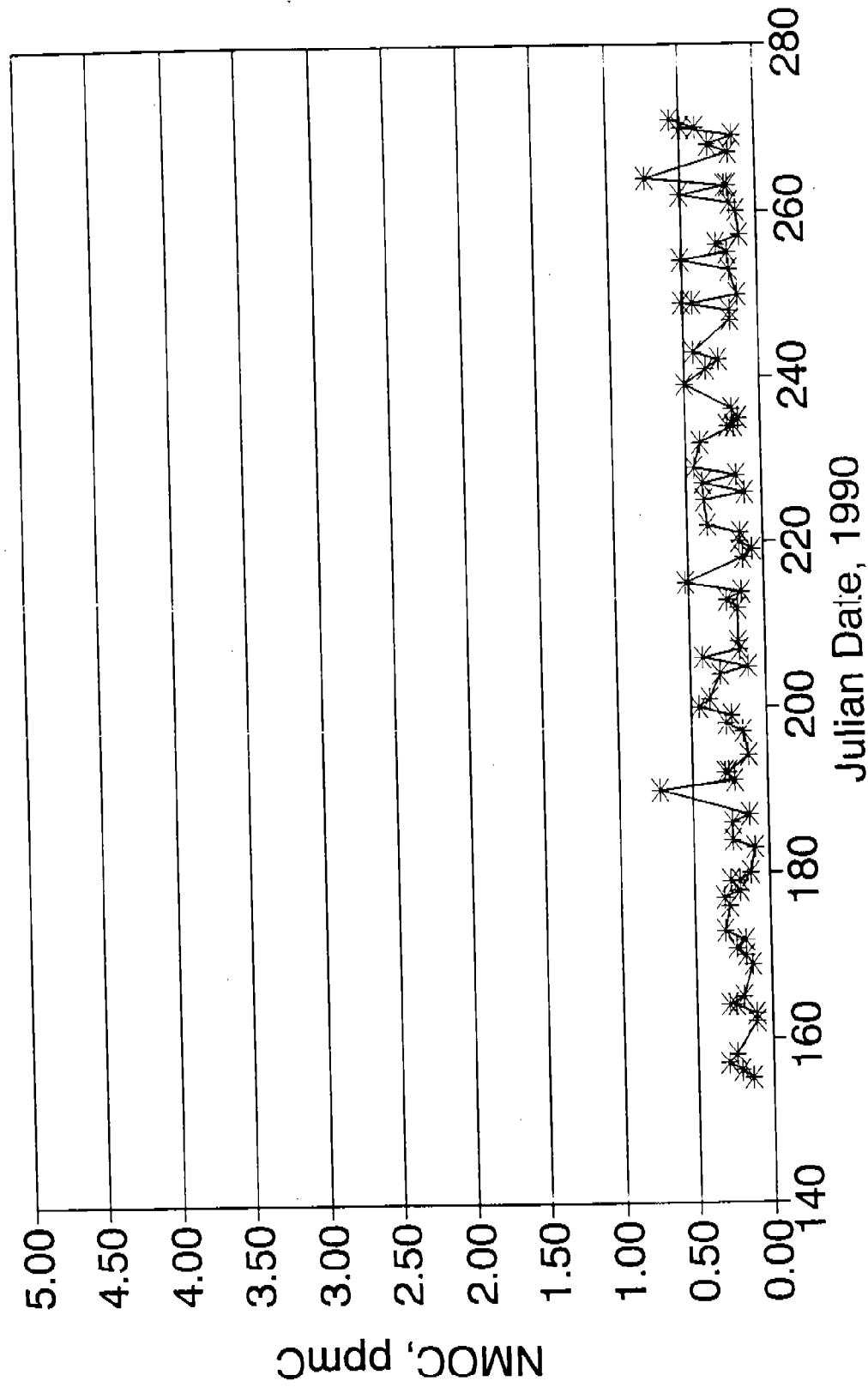


Figure C-3. Plot of NMOC concentration for Hartford, CT.

TABLE C-3. SUMMARY OF THE 1990 NMOC DATA FOR HARTFORD, CT (HTCT)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
04-Jun-90	155	1032	635	19.0	17.0	D	0.135	0.207
05-Jun-90	156	1038	854	19.0	17.0	C	0.205	
06-Jun-90	157	1037	638	18.4	17.5	D	0.293	
07-Jun-90	158	1034	878	11.5	12.0	D	0.233	
11-Jun-90	162	1036	885	16.6	16.5	C	0.104	0.224
12-Jun-90	163	1044	803	19.0	18.5	A	0.097	
13-Jun-90	164	1048	193	19.0	18.0	B	0.235	
13-Jun-90	164	1047	800	19.0	18.0	A	0.276	
14-Jun-90	165	1060	74	18.0	17.0	B	0.184	0.256
18-Jun-90	169	1067	719	19.0	18.0	C	0.116	
19-Jun-90	170	1084	872	17.8	16.0	D	0.168	
20-Jun-90	171	1102	634	25.0	23.0	D	0.226	
21-Jun-90	172	1093	925	18.0	18.0	C	0.159	0.272
22-Jun-90	173	1099	927	19.0	18.0	C	0.305	
25-Jun-90	176	1108	815	18.0	18.0	D	0.272	
26-Jun-90	177	1137	648	18.0	18.0	C	0.298	
27-Jun-90	178	1120	681	27.0	28.0	B	0.193	0.256
28-Jun-90	179	1125	36	17.0	17.0	C	0.254	
28-Jun-90	179	1124	777	18.0	17.0	D	0.198	
29-Jun-90	180	1138	663	18.2	18.0	A	0.125	
02-Jul-90	183	1151	651	18.0	19.0	A	0.089	0.489
03-Jul-90	184	1152	690	18.0	18.0	C	0.241	
05-Jul-90	186	1175	20	17.5	16.0	B	0.239	
06-Jul-90	187	1170	684	18.0	18.0	A	0.119	
09-Jul-90	190	1191	899	26.0	26.0	C	0.718	0.410
10-Jul-90	191	1196	48	18.2	17.0	D	0.215	
11-Jul-90	192	1190	686	18.2	17.0	C	0.275	
11-Jul-90	192	1189	775	18.2	18.0	D	0.254	
13-Jul-90	194	1206	815	17.8	15.0	C	0.124	0.446
16-Jul-90	197	1221	813	18.0	18.0	C	0.152	
17-Jul-90	198	1227	875	17.8	16.0	C	0.270	
18-Jul-90	199	1226	671	18.2	18.0	D	0.231	
19-Jul-90	200	1245	807	18.0	17.0	C	0.443	0.410
20-Jul-90	201	1246	837	17.7	18.0	D	0.371	
23-Jul-90	204	1266	178	18.0	16.0	C	0.298	
24-Jul-90	205	1260	789	18.0	18.0	C	0.109	
25-Jul-90	206	1294	793	17.8	19.0	C	0.421	0.160
26-Jul-90	207	1287	638	18.0	18.0	C	0.165	
27-Jul-90	208	1282	666	18.0	18.0	C	0.173	
27-Jul-90	208	1281	868	18.0	18.0	D	0.177	
31-Jul-90	212	1311	74	17.5	16.0	B	0.177	0.160
01-Aug-90	213	1325	636	18.0	19.0	A	0.243	
02-Aug-90	214	1330	924	17.5	18.0	A	0.146	
03-Aug-90	215	1348	837	18.0	19.0	C	0.518	
06-Aug-90	218	1344	49	17.5	18.0	C	0.133	0.160
07-Aug-90	219	1347	17	30.0	30.0	D	0.066	
08-Aug-90	220	1368	118	30.0	30.0	D	0.157	
09-Aug-90	221	1369	684	18.0	19.0	D	0.147	
10-Aug-90	222	1383	624	20.0	19.0	C	0.361	0.160
13-Aug-90	225	1378	131	17.8	18.0	D	0.382	
14-Aug-90	226	1382	60	18.0	17.0	D	0.106	
15-Aug-90	227	1409	660	20.0	21.0	C	0.394	
16-Aug-90	228	1407	17	18.0	18.0	C	0.160	0.160
17-Aug-90	229	1410	823	17.5	19.0	D	0.445	

TABLE C-3. SUMMARY OF THE 1990 NMOC DATA FOR HARTFORD, CT (HTCI)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
20-Aug-90	232	1408	842	17.8	18.0	D	0.408	
22-Aug-90	234	1424	20	17.0	17.0	D	0.169	
22-Aug-90	234	1428	813	17.0	18.0	D	0.214	
23-Aug-90	235	1432	667	18.0	19.0	C	0.141	
24-Aug-90	236	1439	618	18.0	18.0	A	0.185	
27-Aug-90	239	1454	674	18.0	18.0	A	0.495	
29-Aug-90	241	1473	800	18.0	18.0	A	0.357	
30-Aug-90	242	1471	193	17.0	18.0	A	0.265	
31-Aug-90	243	1474	638	18.0	18.0	C	0.439	
04-Sep-90	247	1497	658	18.0	19.0	C	0.180	
05-Sep-90	248	1496	20	17.0	18.0	D	0.189	
06-Sep-90	249	1511	17	17.0	18.0	C	0.508	
06-Sep-90	249	1512	868	17.0	18.0	D	0.439	
07-Sep-90	250	1514	137	16.0	18.0	C	0.129	0.192
10-Sep-90	253	1541	649	18.0	18.0	C	0.183	
11-Sep-90	254	1536	854	18.0	18.0	B	0.506	
12-Sep-90	255	1551	658	18.0	18.0	B	0.193	
13-Sep-90	256	1558	878	17.0	19.0	D	0.272	0.318
14-Sep-90	257	1557	648	17.0	18.0	C	0.116	0.172
17-Sep-90	260	1586	780	18.0	18.0	B	0.134	
18-Sep-90	261	1585	872	18.0	18.0	A	0.176	
19-Sep-90	262	1591	711	18.0	18.0	C	0.509	
20-Sep-90	263	1594	171	16.0	17.0	C	0.185	
20-Sep-90	263	1595	309	16.0	17.0	D	0.208	
21-Sep-90	264	1612	192	17.0	18.0	A	0.738	
24-Sep-90	267	1617	626	18.0	18.0	C	0.171	
25-Sep-90	268	1636	302	17.0	17.0	B	0.315	
26-Sep-90	269	1635	692	18.0	19.0	D	0.140	
27-Sep-90	270	1633	628	19.0	16.0	C	0.487	
27-Sep-90	270	1634	80	19.0	20.0	D	0.391	
28-Sep-90	271	1637	20	19.0	20.0	C	0.558	

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Long Island, NY

1990 NMOC Program - LINY

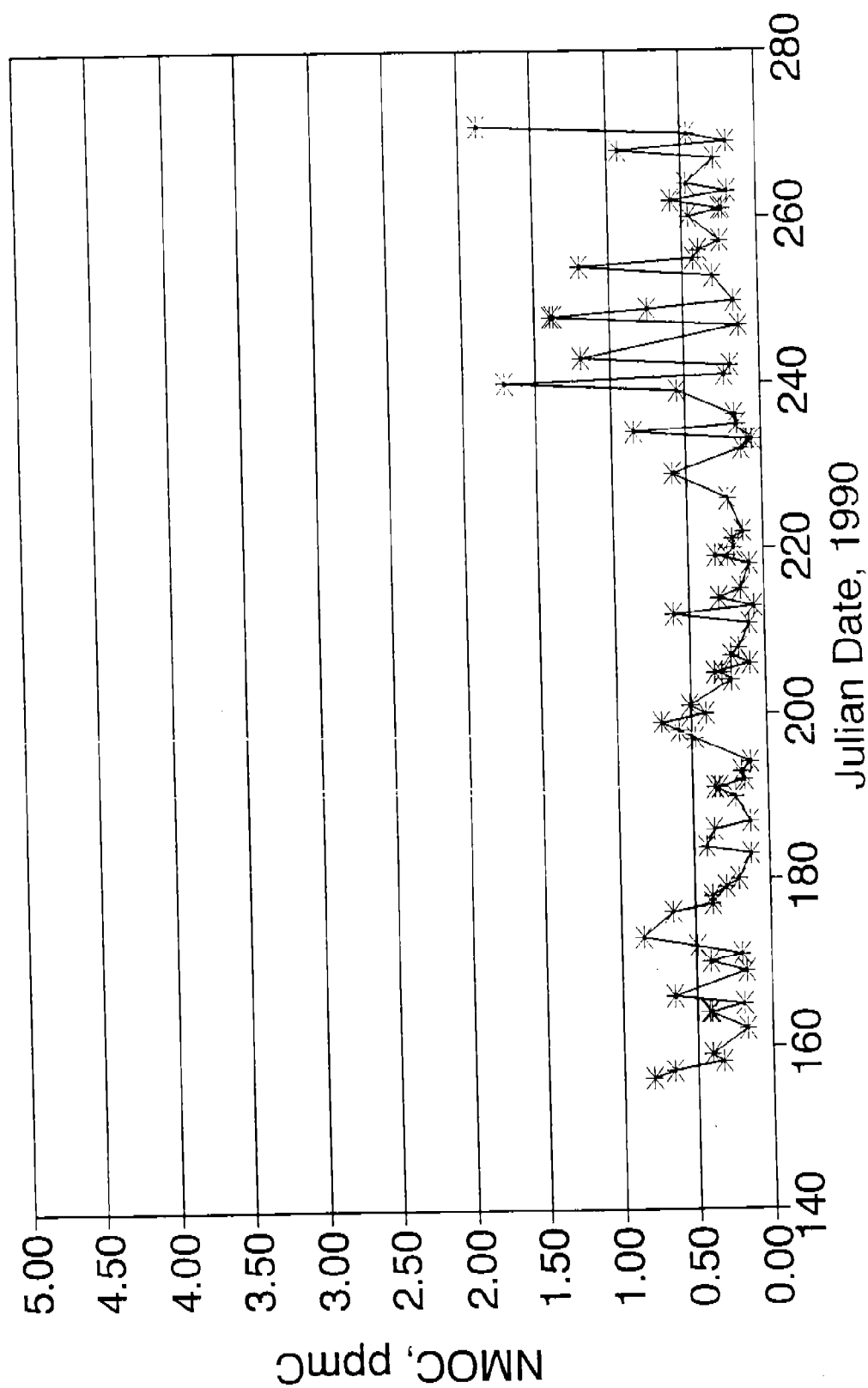


Figure C-4. Plot of NMOC concentration for Long Island, NY .

TABLE C-4. SUMMARY OF THE 1990 NMOC DATA FOR LONG ISLAND, NY (LINY)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
05-Jun-90	156	1002	48	12.3	13.5	C	0.796	
06-Jun-90	157	1020	711	12.0	13.5	A	0.660	0.745
07-Jun-90	158	1019	927	12.0	11.0	B	0.333	0.420
08-Jun-90	159	1021	618	12.0	14.0	A	0.401	0.495
11-Jun-90	162	1041	764	12.0	14.0	B	0.159	
13-Jun-90	164	1045	813	17.0	16.5	A	0.411	
13-Jun-90	164	1046	77	17.0	16.5	B	0.410	
14-Jun-90	165	1058	924	14.0	14.0	B	0.189	
15-Jun-90	166	1055	91	11.8	13.0	A	0.644	
18-Jun-90	169	1085	842	11.5	12.5	C	0.159	0.252
19-Jun-90	170	1081	131	11.5	12.0	D	0.402	
20-Jun-90	171	1083	897	11.4	12.0	D	0.198	
21-Jun-90	172	1097	723	11.8	13.0	C	0.494	
22-Jun-90	173	1101	675	11.8	10.0	C	0.851	0.968
25-Jun-90	176	1119	783	11.9	12.0	A	0.651	
26-Jun-90	177	1132	660	17.0	17.0	B	0.382	
26-Jun-90	177	1133	800	17.0	17.0	A	0.389	
27-Jun-90	178	1116	118	11.7	12.0	A	0.389	
28-Jun-90	179	1139	711	11.9	13.0	B	0.289	0.317
29-Jun-90	180	1136	400	11.8	12.0	B	0.207	
02-Jul-90	183	1154	765	11.6	13.0	C	0.119	
03-Jul-90	184	1158	803	11.8	12.0	D	0.419	
05-Jul-90	186	1156	30	12.0	12.0	D	0.359	
06-Jul-90	187	1185	719	12.0	13.0	A	0.116	
09-Jul-90	190	1183	80	11.6	12.0	B	0.216	
10-Jul-90	191	1187	878	16.4	16.0	B	0.355	
10-Jul-90	191	1188	626	16.2	16.0	B	0.320	
11-Jul-90	192	1212	628	12.0	13.0	D	0.150	
12-Jul-90	193	1211	927	11.6	13.0	C	0.171	0.267
13-Jul-90	194	1210	697	12.3	14.0	D	0.112	0.160
16-Jul-90	197	1231	928	12.2	13.0	C	0.476	
17-Jul-90	198	1232	657	12.2	14.0	D	0.584	0.615
18-Jul-90	199	1234	607	8.0	8.0	D	0.700	
19-Jul-90	200	1254	629	12.1	14.0	C	0.410	0.534
20-Jul-90	201	1257	890	11.6	12.0	D	0.506	
23-Jul-90	204	1253	20	12.5	12.0	D	0.230	
24-Jul-90	205	1270	899	10.0	9.0	A	0.285	
24-Jul-90	205	1271	722	10.1	9.0	B	0.338	
25-Jul-90	206	1276	765	10.9	14.0	B	0.104	
26-Jul-90	207	1296	400	11.8	12.0	A	0.224	
27-Jul-90	208	1298	878	11.6	13.0	A	0.171	0.195
30-Jul-90	211	1324	667	12.0	14.0	D	0.100	
31-Jul-90	212	1323	22	11.4	12.0	C	0.609	0.162
01-Aug-90	213	1318	927	12.0	12.0	C	0.071	
02-Aug-90	214	1335	678	12.0	14.0	C	0.302	
03-Aug-90	215	1340	780	28.5	28.0	D	0.157	
06-Aug-90	218	1341	80	11.5	12.0	D	0.088	
07-Aug-90	219	1359	776	17.0	17.0	C	0.319	
07-Aug-90	219	1364	28	16.5	16.5	D	0.242	
08-Aug-90	220	1365	899	12.3	12.0	C	0.193	
09-Aug-90	221	1647	890	14.0	15.0	D	0.210	
10-Aug-90	222	1394	874	13.0	13.0	C	0.135	0.132
14-Aug-90	226	1398	137	13.0	13.0	C	0.223	
17-Aug-90	229	1419	800	14.0	15.0	A	0.598	

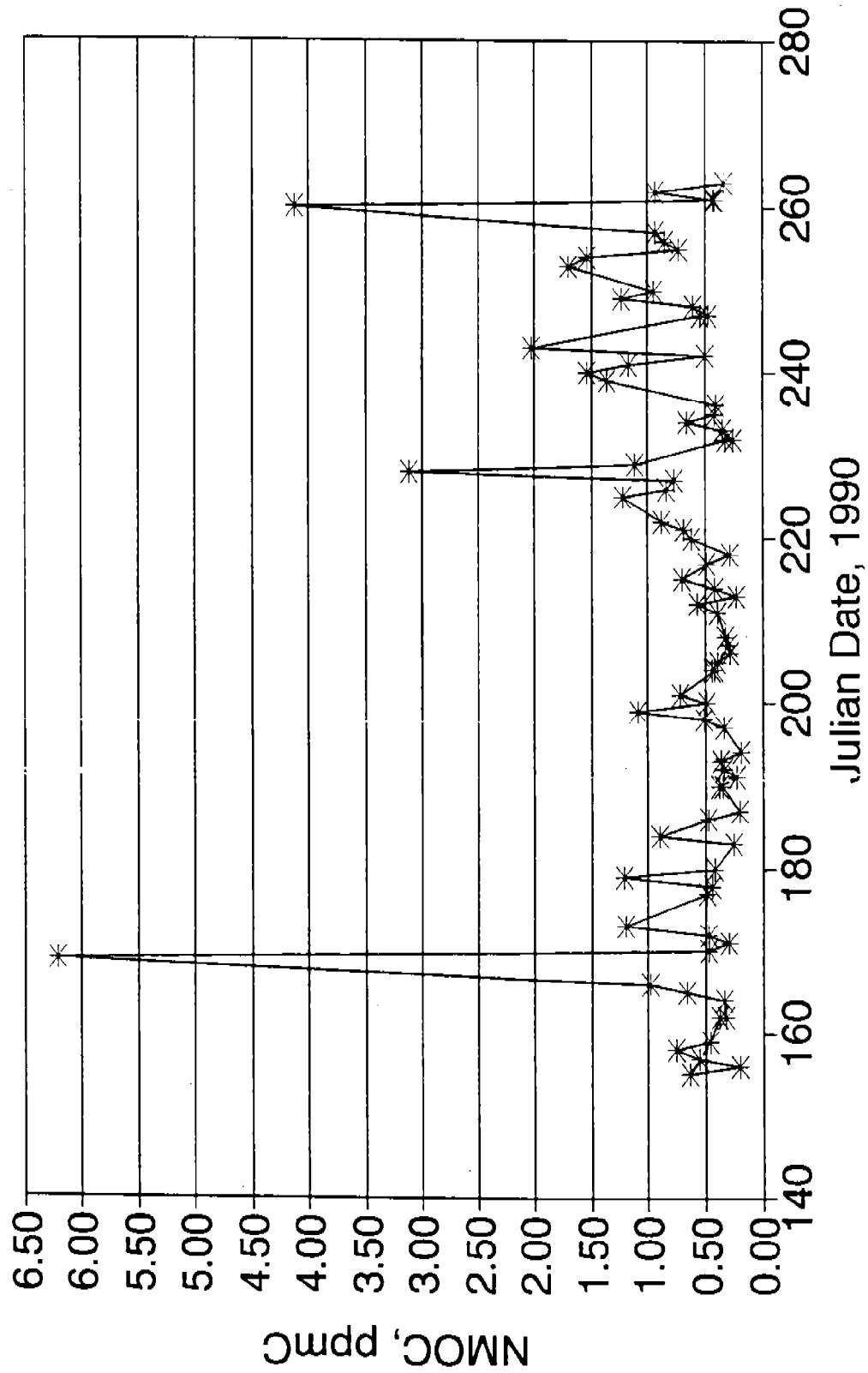
TABLE C-4. SUMMARY OF THE 1990 NMOC DATA FOR LONG ISLAND, NY (LINY)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
20-Aug-90	232	1420	878	13.8	11.0	B	0.128	
21-Aug-90	233	1426	853	17.0	18.0	D	0.060	
21-Aug-90	233	1456	780	17.0	16.0	B	0.088	
22-Aug-90	234	1465	172	14.3	14.0	B	0.848	
23-Aug-90	235	1423	36	13.0	14.0	C	0.153	
24-Aug-90	236	1443	870	17.0	18.0	D	0.170	
27-Aug-90	239	1447	649	14.0	14.0	B	0.551	
28-Aug-90	240	1483	28	22.0	22.0	C	1.710	
29-Aug-90	241	1480	651	13.8	14.0	D	0.236	
30-Aug-90	242	1482	854	13.5	14.0	D	0.190	
31-Aug-90	243	1481	833	13.2	14.0	C	1.190	1.308
04-Sep-90	247	1505	60	14.0	14.0	D	0.133	
05-Sep-90	248	1503	671	23.5	24.0	D	1.371	
05-Sep-90	248	1504	629	23.0	16.0	C	1.392	
06-Sep-90	249	1510	842	16.0	16.0	A	0.743	
07-Sep-90	250	1539	635	13.5	14.0	D	0.162	
10-Sep-90	253	1542	77	28.0	26.0	D	0.298	
11-Sep-90	254	1540	783	14.0	15.0	C	1.200	
12-Sep-90	255	1574	28	13.0	14.0	C	0.427	
13-Sep-90	256	1568	638	14.0	14.0	B	0.398	
14-Sep-90	257	1570	178	14.0	14.0	A	0.245	
17-Sep-90	260	1582	91	12.0	12.0	C	0.460	
18-Sep-90	261	1571	690	19.0	19.0	D	0.228	
18-Sep-90	261	1572	899	19.0	20.0	C	0.246	
19-Sep-90	262	1607	198	13.5	13.0	D	0.575	
20-Sep-90	263	1608	400	13.5	14.0	C	0.190	
21-Sep-90	264	1606	66	14.5	14.0	C	0.465	
24-Sep-90	267	1603	106	13.0	13.0	D	0.281	
25-Sep-90	268	1645	671	15.0	15.0	D	0.916	
26-Sep-90	269	1638	635	14.0	14.0	C	0.195	
27-Sep-90	270	1639	674	14.0	12.0	D	0.457	
28-Sep-90	271	1640	112	14.0	14.0	C	1.867	

Manhattan, NY

1990 NMOC Program - MNY (Expanded)



Manhattan, NY

1990 NMOC Program - MNY

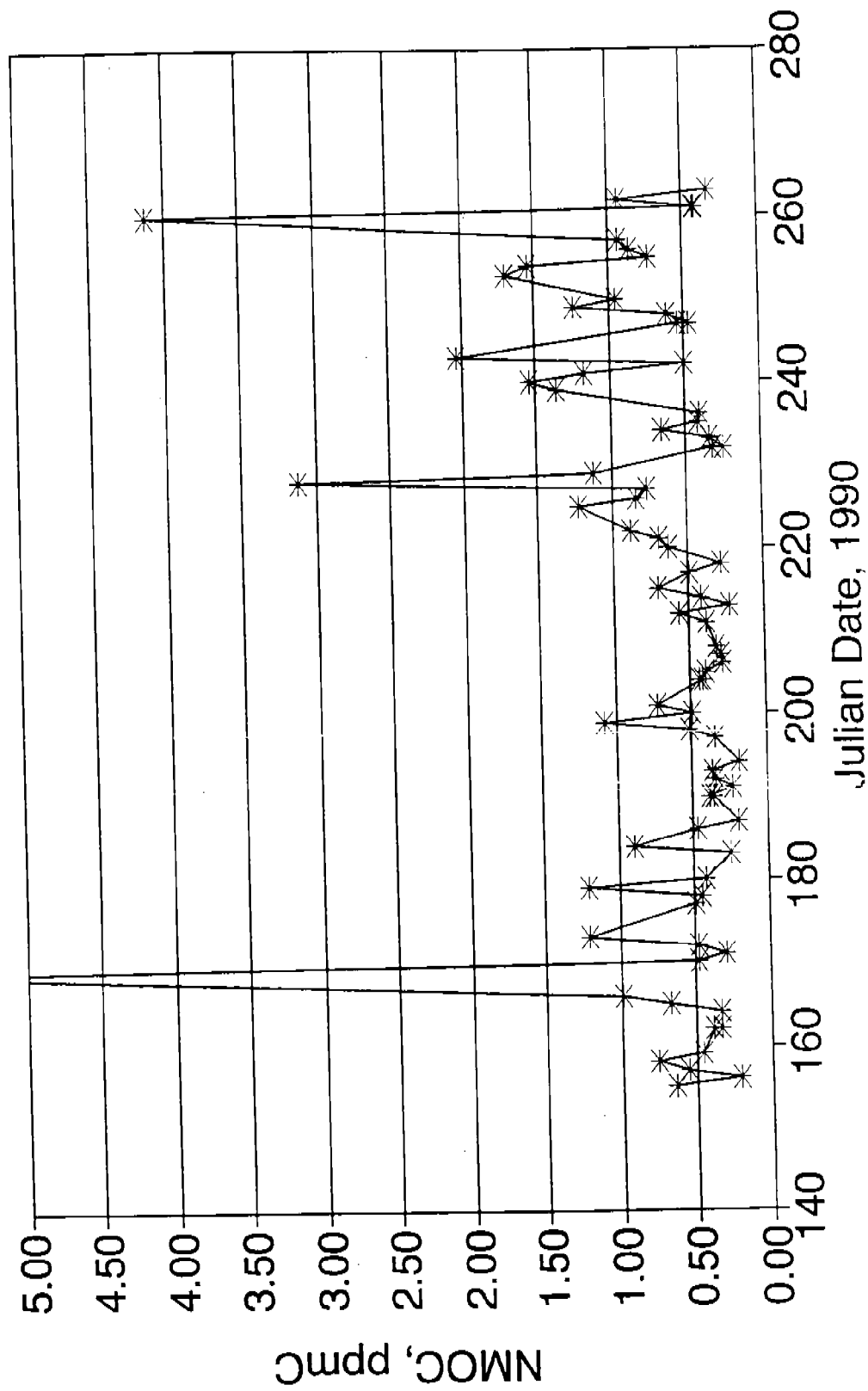


Figure C-5. Plot of NMOC concentration for Manhattan, NY.

TABLE C-5. SUMMARY OF THE 1990 NMOC DATA FOR MANHATTAN, NY (MNY)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
04-Jun-90	155	1003	872	13.0	12.0	B	0.634	
05-Jun-90	156	1072	672	13.0	12.0	C	0.202	
06-Jun-90	157	1013	853	13.0	11.5	A	0.549	
07-Jun-90	158	1015	724	14.0	12.5	C	0.756	
08-Jun-90	159	1022	651	14.0	12.0	B	0.457	
11-Jun-90	162	1026	875	17.0	15.0	C	0.382	
11-Jun-90	162	1027	677	17.0	15.0	D	0.327	0.403
13-Jun-90	164	1043	30	13.0	12.0	B	0.331	0.518
14-Jun-90	165	1049	780	13.0	11.5	C	0.664	
15-Jun-90	166	1059	36	12.0	13.0	A	0.979	
18-Jun-90	169	1071	178	14.0	12.5	C	6.200	
19-Jun-90	170	1077	807	13.0	12.5	A	0.474	
20-Jun-90	171	1082	921	12.5	12.0	C	0.294	
21-Jun-90	172	1087	638	13.0	12.5	B	0.476	0.496
22-Jun-90	173	1098	49	12.0	11.0	D	1.203	
26-Jun-90	177	1113	697	14.0	12.0	C	0.488	
27-Jun-90	178	1117	875	14.0	16.0	B	0.443	
28-Jun-90	179	1126	924	14.0	13.0	D	1.210	1.421
29-Jun-90	180	1134	624	14.0	13.0	A	0.418	0.435
02-Jul-90	183	1147	764	14.0	13.0	D	0.248	0.314
03-Jul-90	184	1167	723	16.0	15.0	B	0.890	
05-Jul-90	186	1186	17	20.0	18.0	A	0.469	0.490
06-Jul-90	187	1177	677	13.0	12.0	B	0.194	
09-Jul-90	190	1180	872	15.0	16.0	C	0.350	
09-Jul-90	190	1178	717	15.0	14.0	C	0.379	0.384
10-Jul-90	191	1182	500	12.3	12.0	B	0.225	0.362
11-Jul-90	192	1201	624	14.0	14.0	D	0.338	
12-Jul-90	193	1200	722	14.0	13.0	C	0.358	
13-Jul-90	194	1209	868	13.0	13.0	C	0.186	
16-Jul-90	197	1228	796	14.0	13.0	D	0.340	
17-Jul-90	198	1233	704	14.0	10.0	C	0.514	
18-Jul-90	199	1236	636	13.0	13.0	D	1.084	
19-Jul-90	200	1239	775	13.0	13.0	C	0.485	0.645
20-Jul-90	201	1247	723	13.0	15.0	C	0.720	
23-Jul-90	204	1259	660	16.0	14.0	D	0.416	0.449
23-Jul-90	204	1258	146	16.0	14.0	C	0.441	
24-Jul-90	205	1264	711	9.0	9.0	C	0.396	
25-Jul-90	206	1272	624	12.0	9.0	A	0.284	
26-Jul-90	207	1288	684	12.0	13.0	D	0.291	
27-Jul-90	208	1291	91	10.0	10.0	B	0.322	0.348
30-Jul-90	211	1303	813	11.0	12.0	D	0.387	
31-Jul-90	212	1314	928	9.0	8.0	B	0.565	
01-Aug-90	213	1319	875	12.3	15.0	D	0.225	
02-Aug-90	214	1331	626	13.0	14.0	B	0.418	
03-Aug-90	215	1334	638	13.0	14.0	C	0.700	0.700
07-Aug-90	217	1346	674	13.0	14.0	C	0.486	
06-Aug-90	218	1336	146	15.0	14.0	D	0.278	
08-Aug-90	220	1649	671	14.0	14.0	D	0.623	0.832
09-Aug-90	221	1366	878	13.0	12.0	D	0.692	
10-Aug-90	222	1372	870	14.0	14.0	B	0.882	
13-Aug-90	225	1373	648	14.0	14.0	C	1.230	
14-Aug-90	226	1392	607	13.0	14.0	C	0.838	
15-Aug-90	227	1396	766	13.0	15.0	C	0.767	
16-Aug-90	228	1404	637	13.0	12.0	D	3.120	3.130

TABLE C-5. SUMMARY OF THE 1990 NMOC DATA FOR MANHATTAN, NY (MNY)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
17-Aug-90	229	1414	685	13.0	15.0	B	1.120	
20-Aug-90	232	1417	666	15.0	15.0	C	0.318	
20-Aug-90	232	1418	193	15.0	15.0	D	0.250	
21-Aug-90	233	1421	783	13.0	12.0	C	0.346	
22-Aug-90	234	1427	690	13.0	15.0	C	0.657	
23-Aug-90	235	1462	704	14.0	14.0	A	0.418	
24-Aug-90	236	1438	711	13.0	13.0	A	0.403	
24-Aug-90	236	1438	711	13.0	14.0	A	1.367	
27-Aug-90	239	1445	717	13.0	14.0	C	1.545	
28-Aug-90	240	1464	678	13.0	13.0	C	1.175	
29-Aug-90	241	1470	878	12.0	12.0	B	0.499	
30-Aug-90	242	1479	685	13.0	14.0	D	2.033	
31-Aug-90	243	1477	54	13.0	13.0	C	0.547	
04-Sep-90	247	1494	885	15.0	16.0	C	0.470	
04-Sep-90	247	1495	91	15.0	16.0	D	0.611	
05-Sep-90	248	1501	648	14.0	14.0	C	1.239	
06-Sep-90	249	1508	690	14.0	25.0	C	0.948	0.862
07-Sep-90	250	1520	684	13.0	13.0	C	1.698	
10-Sep-90	253	1527	113	13.0	13.0	B	1.542	
11-Sep-90	254	1537	828	13.0	13.0	C	0.729	
12-Sep-90	255	1545	111	13.0	13.0	C	0.857	
13-Sep-90	256	1552	618	13.0	13.0	A	0.936	
14-Sep-90	257	1561	60	12.0	12.0	C	4.125	
17-Sep-90	260	1564	629	6.0	13.0	C	0.427	
18-Sep-90	261	1580	783	15.0	15.0	B	0.411	
18-Sep-90	261	1579	649	15.0	15.0	A	0.934	
19-Sep-90	262	1589	684	13.0	14.0	C	0.335	
20-Sep-90	263	1593	77	14.0	12.0	A		

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Newark, NJ

1990 NMOC Program - NWNJ

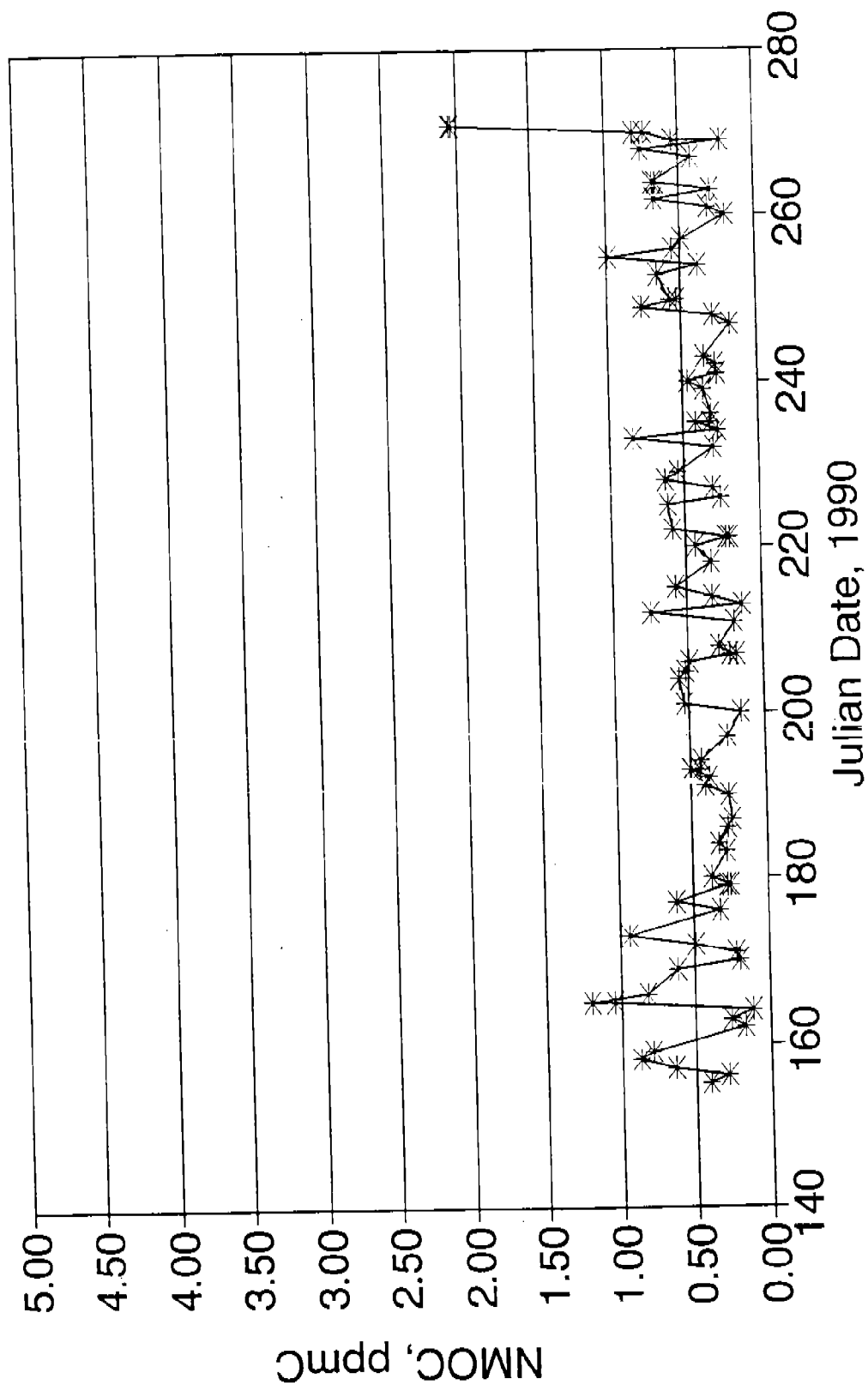


Figure C-6. Plot of NMOC concentration for Newark, NJ.

TABLE C-6. SUMMARY OF THE 1990 NMOC DATA FOR NEWARK, NJ (NWNJ)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
04-Jun-90	155	1010	717	14.1	16.5	B	0.409	
05-Jun-90	156	1008	666	15.1	18.0	B	0.283	
06-Jun-90	157	1007	899	15.0	17.0	D	0.634	0.635
07-Jun-90	158	1014	658	14.3	16.5	D	0.871	
08-Jun-90	159	1025	667	15.0	17.0	D	0.785	
11-Jun-90	162	1028	686	14.4	17.0	C	0.163	0.211
12-Jun-90	163	1040	649	15.0	17.5	A	0.253	0.304
13-Jun-90	164	1052	792	14.5	17.0	D	0.110	0.195
14-Jun-90	165	1061	22	18.3	20.0	C	1.034	
14-Jun-90	165	1062	149	18.3	20.0	D	1.190	
15-Jun-90	166	1070	870	14.0	12.0	D	0.812	
18-Jun-90	169	1075	707	15.9	18.5	A	0.621	
19-Jun-90	170	1076	830	13.6	16.0	B	0.199	
20-Jun-90	171	1091	838	14.0	13.0	A	0.216	
21-Jun-90	172	1107	104	14.5	17.5	A	0.486	
22-Jun-90	173	1090	626	15.0	14.0	B	0.929	
25-Jun-90	176	1106	137	15.4	18.0	D	0.326	0.392
26-Jun-90	177	1109	686	15.0	18.0	C	0.617	
28-Jun-90	179	1128	113	13.2	15.0	D	0.273	
28-Jun-90	179	1129	146	13.0	15.0	D	0.244	
29-Jun-90	180	1144	628	14.0	16.0	D	0.376	
02-Jul-90	183	1143	500	19.5	22.0	C	0.273	
03-Jul-90	184	1157	921	13.0	14.0	C	0.318	
05-Jul-90	186	1176	796	17.8	12.0	A	0.257	
06-Jul-90	187	1164	762	15.0	17.0	B	0.231	
09-Jul-90	190	1169	178	13.9	14.0	B	0.243	
10-Jul-90	191	1195	131	14.2	16.0	C	0.410	
11-Jul-90	192	1194	635	16.0	15.0	D	0.370	
12-Jul-90	193	1204	853	18.1	17.0	C	0.505	
12-Jul-90	193	1205	638	18.1	17.0	D	0.435	
13-Jul-90	194	1225	692	12.4	15.0	C	0.428	
16-Jul-90	197	1229	632	14.0	15.0	C	0.243	
19-Jul-90	200	1275	707	15.5	16.0	B	0.148	
20-Jul-90	201	1248	191	14.0	14.0	D	0.527	0.591
23-Jul-90	204	1263	864	14.1	16.0	D	0.560	
24-Jul-90	205	1240	777	15.5	18.0	D	0.516	
25-Jul-90	206	1273	815	14.4	16.0	B	0.492	
26-Jul-90	207	1285	764	14.0	14.0	C	0.169	
26-Jul-90	207	1286	672	14.0	14.0	C	0.220	
27-Jul-90	208	1305	676	15.2	18.0	C	0.287	0.375
30-Jul-90	211	1295	925	17.0	19.0	D	0.184	
31-Jul-90	212	1312	30	14.0	15.0	B	0.737	
01-Aug-90	213	1326	803	13.4	16.0	B	0.131	
02-Aug-90	214	1338	697	14.0	17.0	C	0.330	
03-Aug-90	215	1339	704	20.2	21.0	C	0.573	
06-Aug-90	218	1648	815	17.0	17.0	C	0.329	
08-Aug-90	220	1371	864	14.0	19.0	A	0.432	
09-Aug-90	221	1370	681	19.0	21.0	B	0.202	
09-Aug-90	221	1385	690	19.0	21.0	A	0.222	
10-Aug-90	222	1380	807	14.3	15.0	D	0.585	
13-Aug-90	225	1390	928	14.8	19.0	C	0.614	
14-Aug-90	226	1391	657	17.0	20.0	D	0.262	
15-Aug-90	227	1400	629	16.2	16.2	B	0.312	
16-Aug-90	228	1412	659	14.5	17.0	D	0.627	

TABLE C-6. SUMMARY OF THE 1990 NMOC DATA FOR NEWARK, NJ (NWNJ)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
17-Aug-90	229	1413	145	11.2	12.0	A	0.544	
20-Aug-90	232	1415	146	12.4	14.0	C	0.302	
21-Aug-90	233	1425	890	14.3	15.0	C	0.835	
22-Aug-90	234	1429	924	14.1	15.0	C	0.273	
23-Aug-90	235	1434	681	18.5	22.0	C	0.411	
23-Aug-90	235	1435	899	18.5	22.0	D	0.320	
24-Aug-90	236	1446	663	13.0	16.0	D	0.315	
27-Aug-90	239	1463	630	12.3	12.0	D	0.366	
28-Aug-90	240	1461	722	12.0	12.0	C	0.464	
29-Aug-90	241	1457	660	12.0	14.0	D	0.266	
30-Aug-90	242	1484	777	12.0	12.0	C	0.283	
31-Aug-90	243	1487	36	13.5	16.0	A	0.355	0.405
04-Sep-90	247	1499	924	8.1	12.0	C	0.171	
05-Sep-90	248	1516	22	12.4	16.0	C	0.289	
06-Sep-90	249	1515	704	16.0	19.0	D	0.758	
07-Sep-90	250	1521	80	19.0	22.0	D	0.531	0.557
07-Sep-90	250	1522	674	19.0	22.0	C	0.569	0.592
10-Sep-90	253	1529	624	0.1	14.0	C	0.658	
11-Sep-90	254	1549	20	14.9	18.0	A	0.385	
12-Sep-90	255	1556	35	13.2	16.0	D	0.988	
13-Sep-90	256	1555	172	14.4	18.0	C	0.550	
14-Sep-90	257	1567	93	13.9	16.0	C	0.489	
17-Sep-90	260	1566	193	15.9	19.0	A	0.193	
18-Sep-90	261	1569	301	16.3	19.0	D	0.315	
19-Sep-90	262	1575	676	17.2	20.0	D	0.670	
20-Sep-90	263	1584	885	15.7	18.0	C	0.295	
21-Sep-90	264	1601	678	18.0	18.0	D	0.660	
21-Sep-90	264	1602	54	18.0	18.0	C	0.677	
24-Sep-90	267	1618	695	17.0	20.0	B	0.413	
25-Sep-90	268	1619	776	17.3	16.0	A	0.753	
26-Sep-90	269	1629	707	18.6	21.0	B	0.211	
26-Sep-90	269	1630	796	18.6	20.0	C	0.541	
27-Sep-90	270	1622	629	16.0	18.0	A	0.728	
27-Sep-90	270	1623	28	18.2	21.0	B	0.808	
28-Sep-90	271	1643	104	18.0	18.0	C	2.033	
28-Sep-90	271	1644	632	18.0	18.0	D	2.046	

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Plainfield, NJ

1990 NMOC Program - PLN

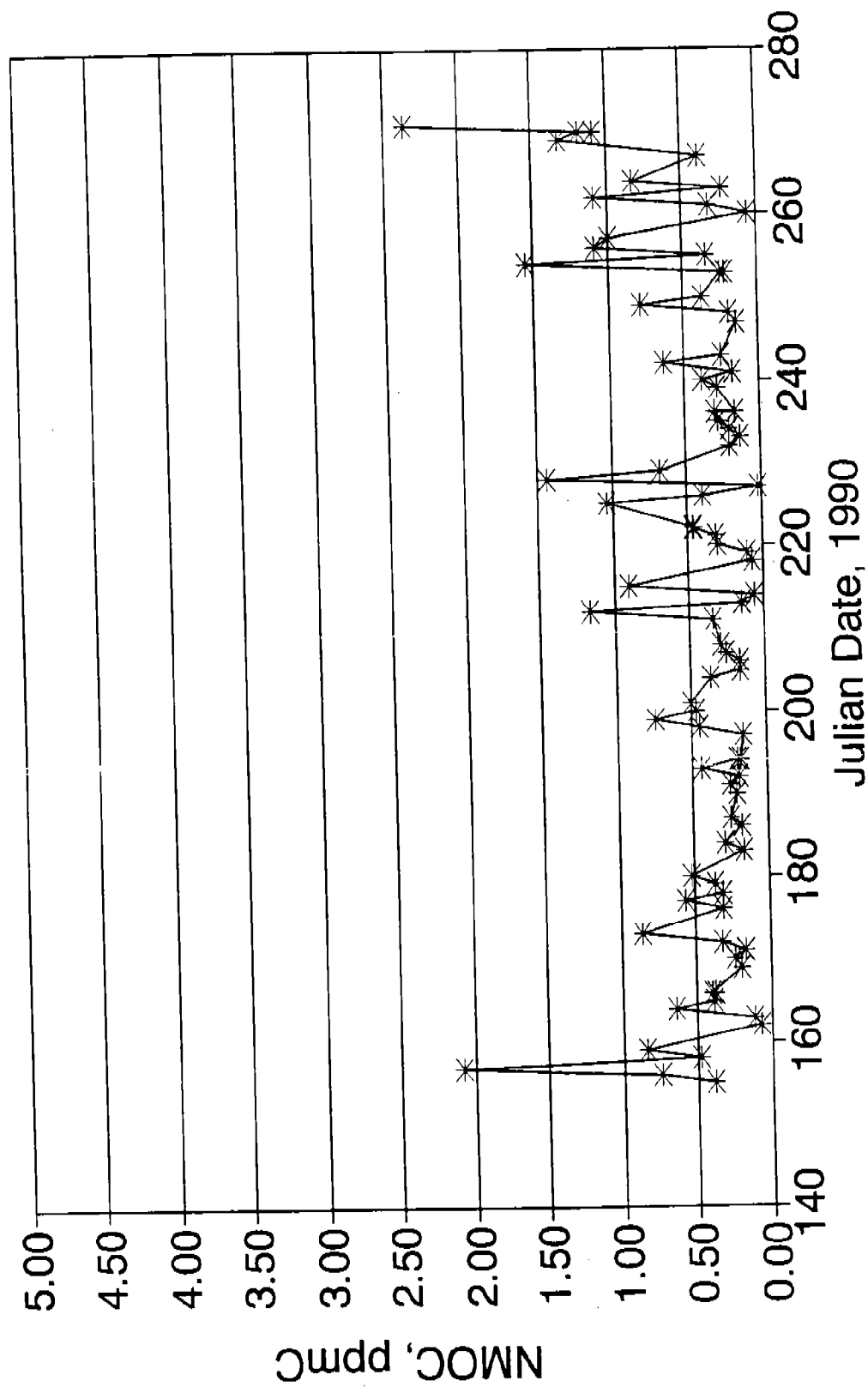


Figure C-7. Plot of NMOC concentration for Plainfield, NJ.

TABLE C-7. SUMMARY OF THE 1990 NMOC DATA FOR PLAINFIELD, NJ (PLNJ)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
04-Jun-90	155	1011	617	18.2	16.0	A	0.381	
05-Jun-90	156	1009	837	18.5	17.5	A	0.746	
06-Jun-90	157	1004	634	19.0	17.0	C	2.074	
07-Jun-90	158	1018	897	18.0	16.0	C	0.476	0.481
08-Jun-90	159	1030	657	19.2	17.0	C	0.836	
11-Jun-90	162	1029	883	18.0	16.0	D	0.069	0.137
12-Jun-90	163	1035	113	18.2	17.0	C	0.106	
13-Jun-90	164	1050	80	18.2	17.0	D	0.636	
14-Jun-90	165	1042	630	18.6	15.5	A	0.387	0.439
15-Jun-90	166	1065	624	15.9	17.0	A	0.378	
15-Jun-90	166	1066	656	15.9	17.0	B	0.399	
18-Jun-90	169	1068	672	18.0	17.0	C	0.196	
19-Jun-90	170	1063	659	18.0	16.5	C	0.241	
20-Jun-90	171	1079	899	17.6	15.0	C	0.159	0.393
21-Jun-90	172	1080	54	17.7	16.0	C	0.317	
22-Jun-90	173	1088	690	18.0	16.5	B	0.862	
25-Jun-90	176	1104	677	18.2	17.0	D	0.313	
26-Jun-90	177	1112	676	18.2	18.0	D	0.561	
27-Jun-90	178	1122	91	17.9	17.0	C	0.309	
28-Jun-90	179	1123	671	18.3	17.0	D	0.360	0.409
29-Jun-90	180	1145	193	14.8	15.0	B	0.516	
29-Jun-90	180	1146	724	14.8	15.0	A	0.516	
02-Jul-90	183	1142	722	18.3	17.0	D	0.161	
03-Jul-90	184	1172	49	18.3	17.0	B	0.285	
05-Jul-90	186	1168	659	19.0	19.0	A	0.173	
06-Jul-90	187	1165	766	17.2	17.5	B	0.244	
09-Jul-90	190	1166	672	17.6	17.0	A	0.208	
10-Jul-90	191	1179	925	17.8	17.0	D	0.250	0.312
11-Jul-90	192	1193	400	18.0	18.0	C	0.188	0.248
12-Jul-90	193	1216	667	18.0	18.0	A	0.433	
13-Jul-90	194	1219	634	14.4	15.0	A	0.194	
13-Jul-90	194	1220	783	14.4	18.0	B	0.175	
16-Jul-90	197	1217	630	17.9	16.0	B	0.156	
17-Jul-90	198	1238	724	18.0	18.0	D	0.443	
18-Jul-90	199	1242	28	18.3	16.0	D	0.742	
19-Jul-90	200	1237	49	17.4	18.0	C	0.466	
20-Jul-90	201	1261	854	17.8	18.0	D	0.502	
23-Jul-90	204	1268	104	17.2	18.0	C	0.363	
24-Jul-90	205	1278	674	16.8	18.0	D	0.163	0.216
25-Jul-90	206	1279	84	17.0	16.0	D	0.162	
26-Jul-90	207	1297	686	18.0	18.0	D	0.256	0.292
27-Jul-90	208	1292	883	14.0	12.0	D	0.289	
27-Jul-90	208	1293	921	14.0	8.0	C	0.286	
30-Jul-90	211	1304	632	17.9	16.0	B	0.339	
31-Jul-90	212	1308	796	17.4	16.0	A	1.165	
01-Aug-90	213	1367	618	17.4	19.0	A	0.143	
02-Aug-90	214	1379	113	20.0	21.0	C	0.061	0.106
03-Aug-90	215	1349	149	17.2	18.0	D	0.899	
06-Aug-90	218	1350	724	19.8	20.0	D	0.066	
07-Aug-90	219	1362	104	14.4	17.0	D	0.102	
08-Aug-90	220	1361	675	17.5	19.0	C	0.301	
09-Aug-90	221	1376	872	17.3	18.0	D	0.308	
10-Aug-90	222	1375	500	13.9	14.0	C	0.464	
10-Aug-90	222	1377	74	13.8	14.0	C	0.454	

TABLE C-7. SUMMARY OF THE 1990 NMOC DATA FOR PLAINFIELD, NJ (PLNJ)

Sample Period: 6:00 a.m. to 9:00 a.m.

Date Sampled	Julian Date Sampled	Sample ID Number	Sample Canister Number	Sample Pressure (psig)	Analysis Pressure (psig)	Radian Channel	Mean NMOC ppmC	QAD NMOC ppmC
13-Aug-90	225	1381	868	17.0	18.0	C	1.040	
14-Aug-90	226	1397	860	17.2	18.0	D	0.400	
15-Aug-90	227	1399	22	20.1	20.0	A	0.012	
16-Aug-90	228	1403	793	17.6	19.0	C	1.440	
17-Aug-90	229	1411	54	17.1	18.0	C	0.682	
20-Aug-90	232	1442	82	17.9	18.0	C	0.201	
21-Aug-90	233	1449	837	17.8	18.0	C	0.128	
22-Aug-90	234	1444	765	17.7	20.0	B	0.210	
23-Aug-90	235	1436	118	17.0	17.0	C	0.282	
24-Aug-90	236	1450	74	14.1	14.5	A	0.297	
24-Aug-90	236	1451	500	14.1	14.5	B	0.164	
27-Aug-90	239	1459	657	18.0	18.0	C	0.278	
28-Aug-90	240	1460	928	18.0	18.0	D	0.387	
29-Aug-90	241	1458	875	18.0	18.0	A	0.170	
30-Aug-90	242	1491	666	17.5	18.0	A	0.635	
31-Aug-90	243	1490	853	17.1	18.0	B	0.250	
04-Sep-90	247	1489	634	18.1	18.0	A	0.141	0.168
05-Sep-90	248	1506	890	17.2	18.0	C	0.198	
06-Sep-90	249	1507	717	17.4	18.0	D	0.779	
07-Sep-90	250	1526	667	17.4	18.0	D	0.375	
10-Sep-90	253	1523	626	10.5	12.0	A	0.252	
10-Sep-90	253	1524	54	13.9	14.0	B	0.214	
11-Sep-90	254	1546	651	17.7	18.0	B	1.550	
12-Sep-90	255	1548	302	17.7	17.0	C	0.346	
13-Sep-90	256	1547	114	16.2	18.0	D	1.089	
14-Sep-90	257	1553	112	16.7	17.0	C	0.996	
17-Sep-90	260	1581	17	16.8	17.0	D	0.057	
18-Sep-90	261	1576	870	19.4	20.0	B	0.321	
19-Sep-90	262	1578	667	19.0	19.5	D	1.089	
20-Sep-90	263	1592	113	18.9	18.0	B	0.226	
21-Sep-90	264	1604	800	19.0	19.0	D	0.822	
24-Sep-90	267	1614	685	19.0	19.0	B	0.380	
26-Sep-90	269	1628	607	18.1	18.0	A	1.325	
27-Sep-90	270	1624	927	14.4	14.0	C	1.189	
27-Sep-90	270	1625	925	14.4	14.0	D	1.092	
28-Sep-90	271	1641	675	14.0	14.0	D	2.363	
28-Sep-90	271	1642	807	14.0	14.0	C	2.364	

APPENDIX D
1990 NMOC MONITORING PROGRAM
INVALIDATED AND MISSING SAMPLES

APPENDIX D

1990 NNOC PROGRAM

VOID OR INVALIDATED SAMPLES - DATE

#	Site	Date	Description	Assigned
1	HTCT	08-Jun-90	Power outage	Equipment
2	MNY	12-Jun-90	System leak	Equipment
3	LINY	12-Jun-90	Double orifice not installed	Operator
4	BMTX	18-Jun-90	Valve open when disconnecting	Operator
5	BMTX	18-Jun-90	Valve open when disconnecting	Operator
6	MNY	25-Jun-90	Valve open when disconnecting	Operator
7	NWNJ	27-Jun-90	Canister leak	Equipment
8	BMTX	28-Jun-90	Power Outage	Equipment
9	BRLA	29-Jun-90	Can valve not opened	Operator
10	LINY	04-Jul-90	Valve open when disconnecting	Operator
11	BRLA	09-Jul-90	Power outage	Equipment
12	NWNJ	17-Jul-90	No pressure	Operator
13	BMTX	02-Aug-90	No sample collected	Operator
14	NWNJ	07-Aug-90	Can valve not opened	Operator
15	BMTX	10-Aug-90	Canister not evacuated	Radian
16	LINY	13-Aug-90	Can valve not opened	Operator
17	LINY	15-Aug-90	Timer misprogrammed	Operator
18	BMTX	17-Aug-90	Can valve not opened	Operator
19	BMTX	20-Aug-90	System leak	Equipment
20	HTCT	21-Aug-90	Can valve not opened	Operator
21	BRLA	21-Aug-90	Power outage	Equipment
22	HTCT	28-Aug-90	High pressure-double orifice used	Operator
23	BRLA	06-Sep-90	Timer misprogrammed	Operator
24	BMTX	13-Sep-90	Can valve not opened	Operator
25	PLNJ	25-Sep-90	Can valve not opened	Operator
26	HTCT	28-Sep-90	Valve opened when disconnecting	Operator

APPENDIX D

1990 NMOC PROGRAM
VOID OR INVALIDATED SAMPLES - SITE

#	Site	Date	Description	Assigned
1	BMTX	18-Jun-90	Valve open when disconnecting	Operator
2	BMTX	18-Jun-90	Valve open when disconnecting	Operator
3	BMTX	28-Jun-90	Power Outage	Equipment
4	BMTX	02-Aug-90	No sample collected	Operator
5	BMTX	10-Aug-90	Canister not evacuated	Radian
6	BMTX	17-Aug-90	Can valve not opened	Operator
7	BMTX	20-Aug-90	System leak	Equipment
8	BMTX	13-Sep-90	Can valve not opened	Operator
9	BRLA	29-Jun-90	Can valve not opened	Operator
10	BRLA	09-Jul-90	Power outage	Equipment
11	BRLA	21-Aug-90	Power outage	Equipment
12	BRLA	06-Sep-90	Timer misprogrammed	Operator
13	HTCT	08-Jun-90	Power outage	Equipment
14	HTCT	21-Aug-90	Can valve not opened	Operator
15	HTCT	28-Aug-90	High pressure-double orifice used	Operator
16	HTCT	28-Sep-90	Valve opened when disconnecting	Operator
17	LINY	12-Jun-90	Double orifice not installed	Operator
18	LINY	04-Jul-90	Valve open when disconnecting	Operator
19	LINY	13-Aug-90	Can valve not opened	Operator
20	LINY	15-Aug-90	Timer misprogrammed	Operator
21	MNY	12-Jun-90	System leak	Equipment
22	MNY	25-Jun-90	Valve open when disconnecting	Operator
23	NWNJ	27-Jun-90	Canister leak	Equipment
24	NWNJ	17-Jul-90	No pressure	Operator
25	NWNJ	07-Aug-90	Can valve not opened	Operator
26	PLNJ	25-Sep-90	Can valve not opened	Operator

APPENDIX E
PDFID INTEGRATOR PROGRAMMING INSTRUCTIONS

INTEGRATOR PROGRAMMING INSTRUCTIONS

Instructions for programming the integrators are as follows.
Be sure to press **ENTER** after each key sequence.

Control Integrator

Oven Temp 90
Oven Temp Limit 405
Oven Temp ON
Oven Temp OFF
List Oven Temp
(A listing should say OvenTemp X°C Setpt 90°C Limit 405°C)
Oven Temp Initial Time 0.20
Oven Temp Initial Value 90
Oven Temp Pgrm Rate 30.00
Oven Temp Final Value 90.00
Oven Temp Final Time 4.00
Oven Temp Equil Time 1.00

Detector A ON
Signal A
Chart speed 4.00
%Offset 10
Zero
Attn 2^ 4

Run Time Annotation ON
Run Table Annotation ON
Clock Table Annotation OFF
Program Annotation OFF
Oven Temp Annotation OFF
Report Annotation OFF

Slave Integrator

Detector B ON
Signal B
Chart speed 4.00
%Offset 10
Zero
Attn 2^ 4

Run Time Annotation ON
Run Table Annotation ON
Clock Table Annotation OFF
Program Annotation OFF
Oven Temp Annotation OFF
(should say ***Warning***Oven Temp now owned by Chnl 2)
Report Annotation OFF

INTEGRATOR PROGRAMMING INSTRUCTIONS (Continued)

Control Integrator

Oven Temp Annotation OFF
(should say ***Warning***Oven Temp now owned by Chnl 1)
Run Time 0.01 Intg OFF
Run Time 0.01 Valve 5 ON
Run Time 0.01 Page
Run Time 0.02 List Attn2^
Run Time 0.04 Oven Temp ON
Run Time 0.20 Valve 2 ON
Run Time 0.21 Valve 2 OFF
Run Time 0.22 Intg ON
Run Time 0.23 Set BL
Run Time 0.23 List Intg
Run Time 1.87 Set BL
Run Time 1.88 Intg OFF
Run Time 1.89 List Intg
Run Time 1.90 Chart Spped 1.5
Run Time 3.44 Valve 2 ON
Run Time 3.45 Valve 2 OFF
Run Time 3.46 Valve 2 ON
Run Time 3.47 Valve 2 OFF
Run Time 3.48 Valve 2 ON
Run Time 3.49 Valve 2 OFF
Run Time 3.50 STOP

Slave Integrator

Run Time 0.01 Intg OFF
Run Time 0.01 Page
Run Time 0.02 List Attn2^
Run Time 0.22 Intg ON
Run Time 0.23 Set BL
Run Time 0.23 List Intg
Run Time 1.87 Set BL
Run Time 1.88 Intg OFF
Run Time 1.89 List Intg
Run Time 1.90 Chart Spped 1.5
Run Time 3.50 STOP

Control Integrator

Det 1 Temp 250
Det 1 Temp Limit 405
Inj 1 Temp 31
Inj 1 Temp Limit 405
Aux 1 Temp 90
Aux 1 Temp Limit 405
Flow A 30
Flow A Limit 500

INTEGRATOR PROGRAMMING INSTRUCTIONS (Continued)

Slave Integrator

Flow B 30
Flow B Limit 500

Control Integrator

Valve 1 OFF
Valve 2 OFF
Valve 3 OFF
Valve 4 OFF
Valve 5 ON
Valve 6 OFF
Valve 7 OFF
Valve 8 OFF
Valve 9 OFF
Valve 10 OFF
Valve 11 OFF
Valve 12 OFF

Threshold 1
Peak Width 0.04

Slave Integrator

Threshold 1
Peak Width 0.04

Control Integrator

20 Valve 5 OFF
25 List Valve 5
30 Oven Temp Initial Value 30
35 Oven Temp OFF
40 Wait 2
60 Start
70 Oven Temp 90
80 Valve 5 ON

Sync ON

APPENDIX F
1990 NMOC DAILY CALIBRATION DATA

TABLE F-1. DAILY CALIBRATION DATA SUMMARY (CHANNEL A)

Cal Date	Julian Cal Date	Initial Zero A.C.	Final Zero A.C.	Initial Zero ppmC	Final Zero ppmC	Initial Cal Factor	Final Cal Factor	Cal Factor Drift	Cal Factor % Drift
06/06/89	157	0.000	0.000	0.003226	0.003226	0.000304	0.000304	0.000000	0.000000
06/08/89	159	0.000	0.000	0.004325	0.001844	0.000305	0.000304	0.000000	0.097962
06/12/89	163	0.000	0.000	0.001551	0.001551	0.000306	0.000306	0.000000	0.000000
06/15/89	166	3.935	3.935	0.001489	0.001333	0.000306	0.000307	-0.000001	-0.329681
06/19/89	170	7.025	7.025	0.001535	0.002268	0.000303	0.000303	-0.000000	-0.129774
06/20/89	171	0.000	0.000	0.002487	0.002691	0.000303	0.000303	-0.000000	-0.080692
06/21/89	172	7.485	7.485	0.002309	0.002334	0.000299	0.000302	-0.000003	-1.110452
06/23/89	174	0.000	0.000	0.001923	0.001923	0.000300	0.000300	0.000000	0.000000
06/27/89	178	15.560	15.560	0.001389	0.001388	0.000297	0.000304	-0.000007	-2.194403
06/29/89	180	4.685	4.685	0.001364	0.000932	0.000299	0.000302	-0.000003	-0.867026
07/03/89	184	5.050	5.050	0.001608	0.000000	0.000299	0.000298	0.000001	0.435590
07/05/89	186	0.000	0.000	0.001865	0.001317	0.000296	0.000294	0.000003	0.846345
07/06/89	187	0.000	0.000	0.001546	0.001149	0.000294	0.000294	0.000001	0.244776
07/10/89	191	6.020	6.020	0.001742	0.001759	0.000294	0.000296	-0.000002	-0.533429
07/11/89	192	0.000	0.000	0.002169	0.002193	0.000294	0.000297	-0.000003	-1.099212
07/12/89	193	0.000	0.000	0.001305	0.000000	0.000293	0.000295	-0.000002	-0.714895
07/18/89	199	0.000	0.000	0.001332	0.001286	0.000293	0.000293	0.000000	0.001611
07/19/89	200	0.000	0.000	0.001370	0.002217	0.000293	0.000296	-0.000003	-1.195837
07/27/89	208	16.175	16.175	0.001072	0.001259	0.000293	0.000297	-0.000004	-1.255266
07/31/89	212	0.705	0.705	0.001157	0.001090	0.000298	0.000299	-0.000001	-0.430754
08/02/89	214	14.725	14.725	0.001674	0.003173	0.000300	0.000296	0.000004	1.273258
08/04/89	216	14.355	14.355	0.001701	0.000201	0.000292	0.000291	0.000002	0.581712
08/09/89	221	21.645	21.645	0.000230	0.002524	0.000293	0.000294	-0.000000	-0.059249
08/11/89	223	5.065	5.065	0.000972	0.003500	0.000292	0.000290	0.000003	0.875000
08/14/89	226	1.380	1.380	0.000000	0.002793	0.000291	0.000293	-0.000002	-0.698089
08/16/89	228	3.900	3.900	0.001154	0.001647	0.000294	0.000295	-0.000001	-0.395674
08/22/89	234	5.060	5.060	0.001533	0.002575	0.000292	0.000297	-0.000005	-1.739579
08/28/89	240	8.315	8.315	0.000798	0.000000	0.000299	0.000295	0.000004	1.416399
08/29/89	241	5.970	4.860	0.001325	0.001434	0.000292	0.000297	-0.000004	-1.516439
08/30/89	242	10.470	10.470	0.001118	0.001118	0.000298	0.000298	0.000000	0.000000
08/31/89	243	2.915	2.915	0.000645	0.000593	0.000294	0.000298	-0.000004	-1.501712
09/05/89	248	2.875	4.480	0.000808	0.001783	0.000295	0.000297	-0.000002	-0.634905
09/06/89	249	2.605	3.425	0.000853	0.004587	0.000296	0.000295	0.000001	0.495894
09/07/89	250	0.000	9.580	0.001061	0.000000	0.000294	0.000296	-0.000003	-0.931626
09/11/89	254	7.275	0.000	0.001485	0.001485	0.000294	0.000294	0.000000	0.000000
09/12/89	255	5.385	5.385	0.001394	0.001170	0.000292	0.000295	-0.000003	-0.981665
09/13/89	256	0.000	0.000	0.001431	0.001407	0.000293	0.000295	-0.000001	-0.475028
09/14/89	257	4.400	4.400	0.001084	0.001084	0.000293	0.000293	0.000000	0.000000
09/15/89	258	6.655	6.655	0.000785	0.001645	0.000293	0.000292	0.000001	0.437559
09/18/89	261	4.040	4.040	0.000624	0.000000	0.000290	0.000292	-0.000002	-0.687442
09/19/89	262	4.780	4.780	0.001048	0.001694	0.000290	0.000290	-0.000001	-0.279998
09/20/89	263	3.240	3.240	0.001694	0.000968	0.000290	0.000289	0.000001	0.381854
09/21/89	264	6.590	6.590	0.001192	0.000000	0.000288	0.000292	-0.000004	-1.402463
09/22/89	265	4.175	4.180	0.000990	0.000990	0.000288	0.000288	0.000000	0.000000
09/26/89	269	5.455	5.455	0.001022	0.001022	0.000290	0.000290	0.000000	0.000000
09/27/89	270	8.030	0.000	0.000734	0.000000	0.000291	0.000295	-0.000003	-1.165454
09/29/89	272	0.000	0.000	0.001010	0.001010	0.000291	0.000291	0.000000	0.000000
09/29/89	272	0.000	0.000	0.001010	0.001010	0.000291	0.000291	0.000000	0.000000
10/02/89	275	0.000	0.000	0.001092	0.001092	0.000288	0.000288	0.000000	0.000000
10/03/89	276	0.000	0.000	0.001011	0.000000	0.000290	0.000291	-0.000002	-0.595562
10/04/89	277	0.000	0.000	0.000680	0.000680	0.000288	0.000288	0.000000	0.000000

TABLE F-2. DAILY CALIBRATION DATA SUMMARY (CHANNEL B)

Cal Date	Julian Cal Date	Initial Zero A.C.	Final Zero A.C.	Initial Zero ppmC	Final Zero ppmC	Initial Cal Factor	Final Cal Factor	Cal Factor Drift	Cal Factor % Drift
06/06/89	157	0.000	0.000	0.000000	0.000000	0.000305	0.000305	0.000000	0.000000
06/07/89	158	0.000	0.000	0.000000	0.000452	0.000305	0.000305	-0.000000	-0.032930
06/12/89	163	0.000	0.000	0.000477	0.000477	0.000309	0.000309	0.000000	0.000000
06/15/89	166	0.000	0.000	0.000000	0.000000	0.000309	0.000310	-0.000001	-0.202326
06/19/89	170	1.750	1.750	0.000188	0.000000	0.000313	0.000312	0.000001	0.409948
06/20/89	171	0.000	0.000	0.000270	0.000681	0.000313	0.000313	-0.000001	-0.249473
06/21/89	172	3.755	3.755	0.000097	0.000098	0.000309	0.000312	-0.000003	-1.066989
06/23/89	174	0.000	0.000	0.000397	0.000397	0.000309	0.000309	0.000000	0.000000
06/27/89	178	3.235	3.235	0.000000	0.000000	0.000309	0.000314	-0.000005	-1.520471
06/29/89	180	0.970	0.970	0.000000	0.000000	0.000309	0.000311	-0.000002	-0.686530
07/03/89	184	1.140	1.140	0.000546	0.000000	0.000307	0.000308	-0.000000	-0.146081
07/05/89	186	0.000	0.000	0.000000	0.000000	0.000307	0.000304	0.000003	0.888594
07/06/89	187	0.000	0.000	0.000000	0.000000	0.000304	0.000302	0.000002	0.597033
07/10/89	191	3.315	3.315	0.000000	0.001747	0.000304	0.000304	0.000000	0.059573
07/11/89	192	0.000	0.000	0.000000	0.000000	0.000305	0.000308	-0.000003	-0.828714
07/12/89	193	0.000	0.000	0.000137	0.000000	0.000305	0.000307	-0.000002	-0.726438
07/18/89	199	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000000	0.000000
07/19/89	200	0.000	0.000	0.000553	0.000987	0.000304	0.000305	-0.000002	-0.526010
07/27/89	208	0.565	0.565	0.000285	0.000000	0.000304	0.000307	-0.000003	-0.831039
07/31/89	212	0.000	0.000	0.000000	0.000000	0.000307	0.000309	-0.000002	-0.594243
08/02/89	214	2.540	2.540	0.000000	0.000827	0.000309	0.000309	-0.000000	-0.060981
08/04/89	216	2.500	2.500	0.000000	0.000000	0.000305	0.000302	0.000003	0.925512
08/09/89	221	6.685	6.685	0.000000	0.000000	0.000301	0.000304	-0.000003	-1.011834
08/11/89	223	0.600	0.600	0.000000	0.000734	0.000301	0.000301	0.000000	0.102413
08/14/89	226	0.980	0.980	0.000000	0.000000	0.000302	0.000303	-0.000002	-0.646297
08/16/89	228	1.755	1.755	0.000000	0.000000	0.000301	0.000302	-0.000001	-0.365781
08/22/89	234	6.160	6.160	0.000190	0.000571	0.000303	0.000308	-0.000005	-1.499200
08/28/89	240	4.040	4.040	0.000604	0.000000	0.000304	0.000308	-0.000004	-1.190001
08/29/89	241	5.340	3.875	0.000000	0.000619	0.000305	0.000305	-0.000000	-0.061877
08/30/89	242	5.915	5.915	0.000000	0.000000	0.000304	0.000304	0.000000	0.000000
08/31/89	243	6.755	6.755	0.000000	0.000000	0.000304	0.000303	0.000001	0.213428
09/05/89	248	1.785	1.360	0.000000	0.000612	0.000305	0.000306	-0.000001	-0.320421
09/06/89	249	1.515	0.535	0.000000	0.000779	0.000304	0.000308	-0.000004	-1.166536
09/08/89	251	1.455	3.785	0.000264	0.000264	0.000304	0.000304	0.000000	0.000000
09/12/89	255	2.860	0.000	0.000000	0.000000	0.000304	0.000306	-0.000002	-0.648759
09/13/89	256	1.350	1.350	0.000000	0.001624	0.000303	0.000304	-0.000001	-0.384231
09/14/89	257	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000000	0.000000
09/15/89	258	4.290	4.290	0.000000	0.000277	0.000303	0.000306	-0.000003	-1.078605
09/18/89	261	5.455	5.455	0.000000	0.000000	0.000299	0.000299	0.000000	0.099762
09/19/89	262	4.210	4.210	0.000000	0.000000	0.000299	0.000298	0.000002	0.503915
09/20/89	263	0.805	0.805	0.000000	0.000000	0.000298	0.000301	-0.000003	-1.115485
09/21/89	264	3.200	3.200	0.000000	0.000000	0.000299	0.000300	-0.000001	-0.302059
09/22/89	265	9.435	9.435	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
09/25/89	268	5.450	6.995	0.000000	0.000000	0.000298	0.000298	0.000000	0.000000
09/27/89	270	3.245	3.245	0.000000	0.000000	0.000304	0.000303	0.000001	0.294636
09/28/89	271	4.905	0.000	0.000000	0.000000	0.000300	0.000300	0.000000	0.000000
09/29/89	272	0.000	0.000	0.000000	0.000000	0.000300	0.000300	0.000000	0.000000
10/02/89	275	0.000	0.000	0.000000	0.000000	0.000297	0.000297	0.000000	0.000000
10/03/89	276	0.000	0.000	0.000000	0.000000	0.000297	0.000301	-0.000004	-1.253519
10/04/89	277	0.000	0.000	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000

TABLE F-3. DAILY CALIBRATION DATA SUMMARY (CHANNEL C)

Cal Date	Julian Cal Date	Initial Zero A.C.	Final Zero A.C.	Initial Zero ppmC	Final Zero ppmC	Initial Cal Factor	Final Cal Factor	Cal Factor Drift	Cal Factor % Drift
06/06/89	157	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000000	0.000000
06/12/89	163	6.630	6.630	0.002016	0.002016	0.000310	0.000310	0.000000	0.000000
06/13/89	164	1.430	1.430	0.000000	0.000000	0.000309	0.000309	-0.000000	-0.108095
06/14/89	165	7.835	7.835	0.000643	0.000000	0.000310	0.000311	-0.000001	-0.300575
06/19/89	170	6.365	6.365	0.000224	0.000000	0.000311	0.000311	0.000001	0.227065
06/20/89	171	0.000	0.000	0.000000	0.001519	0.000311	0.000311	-0.000001	-0.210027
06/22/89	173	4.780	4.780	0.000000	0.000549	0.000311	0.000311	0.000000	0.014707
06/26/89	177	2.390	2.390	0.000581	0.000000	0.000309	0.000311	-0.000002	-0.666836
06/27/89	178	5.965	5.965	0.000000	0.000000	0.000307	0.000309	-0.000001	-0.470070
06/28/89	179	2.040	2.040	0.002196	0.002196	0.000310	0.000310	0.000000	0.000000
07/03/89	184	0.000	0.000	0.000096	0.000000	0.000311	0.000309	0.000002	0.620594
07/05/89	186	0.000	0.000	0.001076	0.001456	0.000308	0.000307	0.000000	0.137097
07/06/89	187	0.000	0.000	0.000117	0.000000	0.000307	0.000307	-0.000000	-0.037251
07/12/89	193	0.000	0.000	0.000222	0.000000	0.000304	0.000306	-0.000002	-0.614882
07/13/89	194	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000000	0.000000
07/17/89	198	0.000	0.000	0.000372	0.001526	0.000304	0.000307	-0.000003	-1.127941
07/17/89	198	0.000	0.000	0.000372	0.001526	0.000304	0.000307	-0.000003	-1.127941
07/19/89	200	0.000	0.000	0.000000	0.000000	0.000306	0.000306	-0.000000	-0.002155
07/20/89	201	0.000	0.000	0.000000	0.000000	0.000306	0.000307	-0.000001	-0.258112
07/21/89	202	0.000	0.000	0.000377	0.000000	0.000305	0.000307	-0.000002	-0.705133
07/24/89	205	0.000	0.000	0.000288	0.001166	0.000303	0.000305	-0.000001	-0.400412
07/25/89	206	0.000	0.000	0.000265	0.001192	0.000307	0.000306	0.000001	0.214445
07/26/89	207	0.000	0.000	0.000426	0.001256	0.000305	0.000307	-0.000001	-0.488261
07/31/89	212	7.020	7.020	0.000000	0.000000	0.000310	0.000311	-0.000001	-0.455049
08/01/89	213	3.385	3.385	0.000000	0.000436	0.000310	0.000307	0.000003	0.889591
08/01/89	213	0.000	0.000	0.000000	0.000436	0.000310	0.000307	0.000003	0.889591
08/03/89	215	1.000	1.000	0.000000	0.000000	0.000310	0.000311	-0.000001	-0.476143
08/07/89	219	0.000	0.000	0.000000	0.000172	0.000304	0.000304	0.000000	0.116014
08/08/89	220	0.000	0.000	0.000000	0.000691	0.000302	0.000306	-0.000004	-1.403917
08/10/89	222	0.000	0.000	0.000000	0.000000	0.000303	0.000299	0.000004	1.279521
08/11/89	223	10.355	10.355	0.000000	0.000000	0.000302	0.000303	-0.000001	-0.337705
08/14/89	226	0.000	0.000	0.000000	0.000875	0.000302	0.000306	-0.000003	-1.106086
08/15/89	227	0.000	0.000	0.000000	0.000316	0.000302	0.000304	-0.000002	-0.753107
08/16/89	228	0.000	0.000	0.000000	0.000000	0.000303	0.000302	0.000001	0.373168
08/17/89	229	12.545	12.545	0.000000	0.001721	0.000303	0.000304	-0.000001	-0.406379
08/18/89	230	4.105	4.105	0.000117	0.000091	0.000295	0.000308	-0.000013	-4.541017
08/21/89	233	1.100	1.100	0.000000	0.000000	0.000306	0.000312	-0.000006	-1.886510
08/23/89	235	5.525	5.525	0.001187	0.000335	0.000306	0.000312	-0.000006	-1.981042
08/24/89	236	6.115	6.115	0.000000	0.000000	0.000311	0.000322	-0.000011	-3.505237
08/25/89	237	2.880	2.880	0.000000	0.001823	0.000307	0.000317	-0.000010	-3.373133
08/29/89	241	1.970	0.000	0.000000	0.000000	0.000307	0.000304	0.000003	1.016790
08/30/89	242	1.515	1.515	0.001056	0.001056	0.000306	0.000306	0.000000	0.000000
09/01/89	244	4.380	4.380	0.000000	0.000000	0.000307	0.000307	0.000000	0.000000
09/05/89	248	6.515	6.070	0.000000	0.005563	0.000308	0.000312	-0.000005	-1.505648
09/06/89	249	2.795	11.635	0.000000	0.000266	0.000303	0.000311	-0.000008	-2.778766
09/07/89	250	1.045	1.045	0.000000	0.000000	0.000307	0.000308	-0.000000	-0.022856
09/08/89	251	0.000	6.580	0.000000	0.000000	0.000307	0.000307	0.000000	0.000000
09/11/89	254	0.000	0.000	0.000000	0.000000	0.000304	0.000304	0.000000	0.000000
09/12/89	255	0.000	0.000	0.000000	0.000000	0.000307	0.000307	0.000000	0.000000
09/13/89	256	0.000	0.000	0.000000	0.000000	0.000303	0.000304	-0.000001	-0.364337
09/14/89	257	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000000	0.000000
09/15/89	258	0.000	0.000	0.000000	0.000400	0.000305	0.000304	0.000001	0.202849
09/18/89	261	2.210	2.760	0.000000	0.000000	0.000299	0.000305	-0.000005	-1.751838
09/19/89	262	0.000	0.000	0.000000	0.000000	0.000302	0.000301	0.000001	0.434796
09/20/89	263	0.000	0.000	0.000000	0.000000	0.000301	0.000302	-0.000001	-0.397107

TABLE F-3. DAILY CALIBRATION DATA SUMMARY (CHANNEL C)

Cal Date	Julian Cal Date	Initial Zero A.C.	Final Zero A.C.	Initial Zero ppmC	Final Zero ppmC	Initial Cal Factor	Final Cal Factor	Cal Factor Drift	Cal Factor Drift
09/21/89	264	1.250	1.250	0.000000	0.000000	0.000301	0.000300	0.000001	-0.410038
09/22/89	265	2.385	2.385	0.000000	0.000000	0.000300	0.000300	0.000000	0.000000
09/24/89	267	0.000	0.570	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
09/25/89	268	0.000	0.000	0.000000	0.000000	0.000298	0.000298	0.000000	0.000000
09/26/89	269	0.000	0.000	0.000000	0.000000	0.000301	0.000301	0.000000	0.000000
09/27/89	270	0.000	0.000	0.000000	0.000000	0.000302	0.000305	-0.000002	-0.807703
09/28/89	271	0.000	0.000	0.000000	0.000000	0.000300	0.000300	0.000000	0.000000
09/29/89	272	0.000	0.000	0.000000	0.000000	0.000302	0.000302	0.000000	0.000000
10/02/89	275	2.515	2.515	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
10/03/89	276	0.000	0.000	0.000000	0.000000	0.000301	0.000302	-0.000002	-0.534528
10/04/89	277	0.000	0.000	0.000000	0.000000	0.000300	0.000300	0.000000	0.000000

TABLE F-4. DAILY CALIBRATION DATA SUMMARY (CHANNEL D)

Cal Date	Julian Cal Date	Initial Zero A.C.	Final Zero A.C.	Initial Zero ppmC	Final Zero ppmC	Initial Cal Factor	Final Cal Factor	Cal Factor Drift	Cal Factor % Drift
06/06/89	157	0.000	0.000	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
06/07/89	158	9.260	9.260	0.001374	0.000000	0.000313	0.000302	0.000010	3.350653
06/08/89	159	0.000	0.000	0.000000	0.000000	0.000304	0.000304	0.000001	0.272276
06/09/89	160	0.000	0.000	0.000000	0.000135	0.000302	0.000300	0.000002	0.671377
06/12/89	163	3.510	3.510	0.002253	0.002253	0.000308	0.000308	0.000000	0.000000
06/13/89	164	0.000	0.000	0.001342	0.000000	0.000307	0.000311	-0.000005	-1.509456
06/14/89	165	6.190	6.190	0.000000	0.000000	0.000307	0.000308	-0.000001	-0.294841
06/15/89	166	8.135	8.135	0.000000	0.000149	0.000307	0.000310	-0.000003	-0.942282
06/16/89	167	0.000	0.000	0.000000	0.000000	0.000306	0.000306	0.000000	0.000000
06/19/89	170	1.845	1.845	0.000000	0.000000	0.000310	0.000309	0.000000	0.111115
06/22/89	173	0.370	0.370	0.000000	0.000618	0.000307	0.000307	0.000000	0.136536
06/23/89	174	0.505	0.505	0.000000	0.000000	0.000308	0.000308	0.000000	0.000000
06/26/89	177	0.000	0.000	0.000000	0.000000	0.000308	0.000307	0.000001	0.196775
06/29/89	180	0.000	0.000	0.000011	0.000363	0.000306	0.000309	-0.000003	-1.003048
07/03/89	184	0.000	0.000	0.000000	0.000000	0.000306	0.000305	0.000001	0.307133
07/05/89	186	0.000	0.000	0.000689	0.001542	0.000305	0.000304	0.000002	0.540610
07/06/89	187	0.000	0.000	0.001627	0.002320	0.000304	0.000304	0.000000	0.131631
07/10/89	191	0.000	0.000	0.000000	0.000000	0.000302	0.000304	-0.000002	-0.638951
07/11/89	192	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000001	0.195601
07/12/89	193	0.000	0.000	0.000000	0.000000	0.000302	0.000303	-0.000001	-0.416619
07/13/89	194	0.000	0.000	0.000066	0.000066	0.000300	0.000300	0.000000	0.000000
07/14/89	195	0.000	0.000	0.000000	0.000000	0.000303	0.000303	0.000000	0.113669
07/17/89	198	0.000	0.000	0.000163	0.001426	0.000302	0.000304	-0.000001	-0.475004
07/18/89	199	13.320	13.320	0.000000	0.000000	0.000302	0.000302	0.000000	0.000000
07/20/89	201	0.000	0.000	0.000000	0.000035	0.000301	0.000302	-0.000000	-0.144582
07/21/89	202	0.000	0.000	0.000000	0.001186	0.000301	0.000305	-0.000004	-1.201915
07/25/89	206	0.000	0.000	0.000000	0.001479	0.000303	0.000303	0.000000	0.083444
07/28/89	209	0.000	0.000	0.000000	0.000000	0.000307	0.000307	0.000000	0.000000
07/31/89	212	0.000	0.000	0.000000	0.000000	0.000307	0.000310	-0.000003	-0.901830
08/02/89	214	0.000	0.000	0.001788	0.000000	0.000305	0.000307	-0.000002	-0.657493
08/03/89	215	13.285	13.285	0.000000	0.000000	0.000307	0.000308	-0.000001	-0.358708
08/04/89	216	0.000	0.000	0.000000	0.000925	0.000300	0.000303	-0.000004	-1.208061
08/06/89	218	0.000	0.000	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
08/07/89	219	0.000	0.000	0.000000	0.000000	0.000300	0.000300	0.000000	0.029398
08/08/89	220	0.865	0.865	0.000000	0.000697	0.000299	0.000301	-0.000002	-0.616333
08/09/89	221	0.405	0.405	0.000000	0.000000	0.000301	0.000302	-0.000001	-0.336481
08/10/89	222	0.000	0.000	0.000000	0.000000	0.000300	0.000303	-0.000003	-1.107990
08/14/89	226	0.000	0.000	0.000000	0.000000	0.000300	0.000306	-0.000006	-1.855203
08/15/89	227	5.695	5.695	0.000000	0.001132	0.000299	0.000305	-0.000006	-1.921009
08/16/89	228	0.000	0.000	0.000000	0.000000	0.000299	0.000302	-0.000002	-0.779748
08/18/89	230	2.905	0.000	0.000000	0.000000	0.000306	0.000292	0.000014	4.460500
08/21/89	233	0.000	0.000	0.000000	0.000000	0.000294	0.000298	-0.000004	-1.423636
08/23/89	235	8.345	8.345	0.000000	0.000174	0.000297	0.000302	-0.000004	-1.498292
08/24/89	236	2.210	0.000	0.000000	0.000000	0.000303	0.000309	-0.000006	-2.056354
08/25/89	237	8.530	0.435	0.000000	0.000000	0.000305	0.000312	-0.000006	-2.074276
08/28/89	240	2.380	2.380	0.000538	0.000000	0.000302	0.000304	-0.000002	-0.588713
08/29/89	241	0.000	1.000	0.000000	0.002642	0.000303	0.000297	0.000005	1.816768
08/30/89	242	0.000	0.000	0.003872	0.003872	0.000304	0.000304	0.000000	0.000000
08/31/89	243	1.370	0.000	0.000000	0.000000	0.000302	0.000308	-0.000006	-1.993487
09/01/89	244	0.000	0.000	0.000109	0.000109	0.000303	0.000303	0.000000	0.000000
09/05/89	248	0.000	0.000	0.000000	0.000665	0.000304	0.000311	-0.000007	-2.357163
09/06/89	249	0.000	0.000	0.000000	0.000116	0.000303	0.000310	-0.000006	-2.121072
09/07/89	250	0.990	2.600	0.000000	0.000000	0.000303	0.000304	-0.000001	-0.327210
09/08/89	251	0.000	0.000	0.000000	0.000000	0.000304	0.000304	0.000000	0.000000
09/11/89	254	1.135	1.135	0.000000	0.000000	0.000302	0.000302	0.000000	0.000000
09/12/89	255	0.000	0.000	0.000000	0.000000	0.000303	0.000303	-0.000001	-0.205518
09/13/89	256	0.340	0.340	0.000000	0.000000	0.000309	0.000309	0.000000	0.023649

TABLE F-4. DAILY CALIBRATION DATA SUMMARY (CHANNEL D)

Cal Date	Julian Cal Date	Initial Zero A.C.	Final Zero A.C.	Initial Zero ppmC	Final Zero ppmC	Initial Cal Factor	Final Cal Factor	Cal Factor Drift	Cal Factor % Drift
09/15/89	258	0.000	0.000	0.000000	0.000000	0.000303	0.000303	-0.000001	-0.185613
09/18/89	261	0.000	0.000	0.000000	0.000000	0.000299	0.000302	-0.000003	-1.101487
09/19/89	262	0.000	0.000	0.000000	0.000000	0.000300	0.000298	0.000002	0.784490
09/20/89	263	7.085	0.000	0.000000	0.000000	0.000298	0.000301	-0.000003	-1.012285
09/21/89	264	0.000	0.000	0.000000	0.000000	0.000298	0.000297	0.000000	0.154848
09/22/89	265	0.000	0.000	0.000000	0.000000	0.000297	0.000297	0.000000	0.000000
09/24/89	267	8.480	8.480	0.000000	0.000000	0.000297	0.000297	0.000000	0.000000
09/25/89	268	0.000	0.000	0.000000	0.000000	0.000296	0.000296	0.000000	0.000000
09/26/89	269	0.000	0.000	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
09/27/89	270	0.000	0.000	0.000000	0.000000	0.000300	0.000303	-0.000004	-1.190461
09/28/89	271	0.000	0.000	0.000000	0.000000	0.000297	0.000297	0.000000	0.000000
09/29/89	272	0.000	0.000	0.000000	0.000000	0.000299	0.000299	0.000000	0.000000
10/02/89	275	0.000	0.000	0.000000	0.000000	0.000297	0.000297	0.000000	0.000000
10/03/89	276	0.000	0.000	0.000000	0.000000	0.000296	0.000299	-0.000003	-0.970956
10/04/89	277	0.000	0.000	0.000000	0.000000	0.000296	0.000296	0.000000	0.000000

APPENDIX G

1990 NMOC IN-HOUSE QUALITY CONTROL SAMPLES

TABLE G-1. NMOC INHOUSE QUALITY CONTROL SAMPLES (CHANNEL A)

Date Analyzed	Julian Date Analyzed	QC I.D. Number	Calculated NMOC ppmC	Measured NMOC ppmC	NMOC Bias ppmC	NMOC Percent Bias
08-Jun-90	159	1001	0.5960	0.6650	0.0690	11.5772
24-Jul-90	205	1213	1.4640	1.6000	0.1360	9.2896
02-Aug-90	214	1306	0.2370	0.2770	0.0400	16.8776
06-Aug-90	218	1307	0.3530	0.3650	0.0120	3.3994
31-Aug-90	243	1468	1.1080	1.1204	0.0124	1.1191

TABLE G-2. NMOC INHOUSE QUALITY CONTROL SAMPLES (CHANNEL B)

Date Analyzed	Julian Date Analyzed	QC I.D. Number	Calculated NMOC ppmC	Measured NMOC ppmC	NMOC Bias ppmC	NMOC Percent Bias
08-Jun-90	159	1001	0.596	0.653	0.057	9.564
24-Jul-90	205	1213	1.464	1.520	0.056	3.825
02-Aug-90	214	1306	0.237	0.279	0.042	17.722
06-Aug-90	218	1307	0.353	0.362	0.009	2.550
31-Aug-90	243	1468	1.108	1.183	0.075	6.760

TABLE G-3. NMOC INHOUSE QUALITY CONTROL SAMPLES (CHANNEL C)

Date Analyzed	Julian Date Analyzed	QC I.D. Number	Calculated NMOC ppmC	Measured NMOC ppmC	NMOC Bias ppmC	NMOC Percent Bias
07-Jun-90	158	1000C	0.45	0.432	-0.018	-4.000
14-Jun-90	165	1031C	0.968	0.957	-0.011	-1.136
24-Jul-90	205	1213C	1.584	1.464	-0.120	-7.576
12-Aug-90	224	1315C	0.58	0.564	-0.016	-2.759
07-Sep-90	250	1498C	1.37	0.796	-0.574	-41.898

TABLE G-4. NMOC INHOUSE QUALITY CONTROL SAMPLES (CHANNEL D)

Date Analyzed	Julian Date Analyzed	QC I.D. Number	Calculated NMOC ppmC	Measured NMOC ppmC	NMOC Bias ppmC	NMOC Percent Bias
07-Jun-90	158	1000	0.459	0.432	-0.027	-5.882
14-Jun-90	165	1031	0.958	0.957	-0.001	-0.104
24-Jul-90	175	1213	1.480	1.464	-0.016	-1.081
12-Aug-90	224	1315	0.563	0.564	0.001	0.178
07-Sep-90	250	1498	1.501	0.796	-0.705	-46.969

APPENDIX H
MULTIPLE DETECTOR SPECIATED THREE-HOUR SITE DATA SUMMARIES

APPENDIX H -- LIST OF TABLES

<u>Table</u>	<u>Page</u>
H-1 MULTIPLE DETECTOR SPECIATED THREE-HOUR DATA SUMMARY FOR BRLA	H-1
H-2 MULTIPLE DETECTOR SPECIATED THREE-HOUR DATA SUMMARY FOR NWNJ	H-4
H-3 MULTIPLE DETECTOR SPECIATED THREE-HOUR DATA SUMMARY FOR PLNJ	H-6

TABLE H-1. MULTIPLE DETECTOR SPECIATED THREE HOUR DATA SUMMARY FOR BRLA

Sample ID	1274	1283	1300	1309D	1310D
Sample Date	7-25-90	7-27-90	7-30-90	7-31-90	7-31-90
Total NMOC, ppmC	0.148	0.383	1.416	0.766	0.740
Compound	Concentration, ppbv				
Acetylene					
1,3-Butadiene	3.010 (H)		6.830 (M)	6.160 (H)	5.940 (H)
Vinyl chloride					
Chloromethane					
Chloroethane					
Bromomethane					
Methylene chloride					
trans-1,2-Dichloroethylene			0.720 (M)		
1,1-Dichloroethane					
Chloroprene		0.690 (M)	1.510 (M)	0.910 (H)	0.510 (H)
Bromochloromethane					
Chloroform	0.723 (M)				
1,1,1-Trichloroethane	0.415 (L)	0.372 (L)	0.286 (L)	0.446 (L)	0.506 (L)
Carbon tetrachloride	0.276 (L)	0.142 (L)	0.177 (L)	0.166 (L)	0.175 (L)
1,2-Dichloroethane					
Benzene	2.930 (H)	1.200 (H)	5.920 (H)	2.720 (H)	3.090 (H)
Trichloroethylene					
1,2-Dichloropropane	1.140 (L)			1.460 (L)	1.400 (H)
Bromodichloromethane					
Toluene	5.680 (H)	2.320 (L)	6.140 (M)	3.900 (H)	3.560 (M)
n-Octane	0.340 (H)			0.460 (H)	
cis-1,3-Dichloropropylene					
1,1,2-Trichloroethane		4.700 (M)			5.060 (H)
Tetrachloroethylene	0.156 (M)		0.147 (L)	0.076 (L)	0.067 (L)
Dibromochloromethane					
Chlorobenzene					
Ethylbenzene	0.660 (L)	0.360 (M)	0.540 (H)	0.390 (M)	0.320 (H)
m/p-Xylene	3.100 (L)	1.600 (M)	2.300 (H)	1.420 (H)	1.380 (H)
Styrene/o-Xylene	1.750 (L)	0.860 (M)	1.100 (H)	0.860 (H)	0.830 (H)
Bromoform					
1,1,2,2-Tetrachloroethane					
m-Dichlorobenzene		0.030 (M)	0.050 (L)	0.040 (L)	
p-Dichlorobenzene		0.300 (L)			
o-Dichlorobenzene					
Propylene	19.410 (L)	2.630 (L)	20.600 (L)	10.310 (L)	9.850 (L)
trans-1,3-Dichloropropylene			2.690 (L)		
H High confidence level	M Medium confidence level	L Low confidence level	(Continued)		

TABLE H-1. BRLA (Continued)

Sample ID	1310R	1322	1324	1333	1351
Sample Date	7-31-90	8-1-90	8-2-90	8-2-90	8-6-90
Total NMOC, ppmC	0.740	0.487	0.100	0.989	0.954
Compound	Concentration, ppbv				
Acetylene					
1,3-Butadiene	5.890 (H)	0.440 (H)		1.780 (H)	3.150 (H)
Vinyl chloride					
Chloromethane					
Chloroethane					
Bromomethane					
Methylene chloride					
trans-1,2-Dichloroethylene			0.310 (H)		
1,1-Dichloroethane					
Chloroprene		0.420 (L)		1.780 (H)	
Bromochloromethane					
Chloroform					0.370 (H)
1,1,1-Trichloroethane	0.516 (L)	0.392 (L)	0.419 (L)	0.502 (L)	0.324 (L)
Carbon tetrachloride	0.174 (L)	0.168 (L)	0.144 (L)	0.300 (L)	0.199 (L)
1,2-Dichloroethane					
Benzene	3.220 (H)	2.670 (H)	2.270 (H)	4.100 (H)	2.300 (H)
Trichloroethylene					
1,2-Dichloropropane	1.380 (H)		1.140 (H)		0.910 (M)
Bromodichloromethane					
Toluene	3.610 (M)	4.640 (M)	4.110 (H)	8.180 (H)	4.220 (M)
n-Octane					
cis-1,3-Dichloropropylene					
1,1,2-Trichloroethane			4.230 (H)		
Tetrachloroethylene	0.083 (L)	1.677 (L)	0.445 (M)	0.532 (L)	0.130 (L)
Dibromochloromethane					
Chlorobenzene	0.080 (L)				
Ethylbenzene	0.300 (H)	0.520 (L)	0.500 (L)	0.980 (H)	0.470 (L)
m/p-Xylene	1.360 (H)	2.660 (L)	3.040 (L)	4.810 (H)	1.870 (L)
Styrene/o-Xylene	0.870 (H)	1.320 (L)	1.570 (L)	2.610 (H)	1.100 (L)
Bromoform					
1,1,2,2-Tetrachloroethane					
m-Dichlorobenzene					
p-Dichlorobenzene	1.520 (L)	0.490 (L)			
o-Dichlorobenzene					
Propylene	9.020 (L)	8.240 (L)	6.230 (L)	12.540 (L)	11.760 (L)
trans-1,3-Dichloropropylene					0.730 (L)
H High confidence level	M Medium confidence level	L Low confidence level	(Continued)		
D Duplicate sample	R Replicate sample				

TABLE H-1. BRLA (Continued)

Sample ID	1352
Sample Date	8-7-90
Total NMOC, ppmC	0.860
Compound	Concentration, ppbv
Acetylene	
1,3-Butadiene	
Vinyl chloride	
Chloromethane	
Chloroethane	
Bromomethane	
Methylene chloride	
trans-1,2-Dichloroethylene	0.410 (M)
1,1-Dichloroethane	
Chloroprene	0.260 (M)
Bromochloromethane	
Chloroform	
1,1,1-Trichloroethane	0.345 (L)
Carbon tetrachloride	0.140 (L)
1,2-Dichloroethane	
Benzene	1.000 (H)
Trichloroethylene	
1,2-Dichloropropane	
Bromodichloromethane	
Toluene	1.760 (L)
n-Octane	
cis-1,3-Dichloropropylene	
1,1,2-Trichloroethane	
Tetrachloroethylene	0.054 (L)
Dibromochloromethane	
Chlorobenzene	
Ethylbenzene	0.250 (L)
m/p-Xylene	0.860 (L)
Styrene/o-Xylene	0.570 (L)
Bromoform	
1,1,2,2-Tetrachloroethane	
m-Dichlorobenzene	
p-Dichlorobenzene	
o-Dichlorobenzene	
Propylene	9.270 (L)
trans-1,3-Dichloropropylene	
H High confidence level	M Medium confidence level
	L Low confidence level

TABLE H-2. MULTIPLE DETECTOR SPECIATED THREE-HOUR DATA SUMMARY FOR NWNJ

Sample ID	1285D	1285R	1286D	1295	1312
Sample Date	7-26-90	7-26-90	7-26-90	7-30-90	7-31-90
Total NMOC, ppmC	0.169	0.169	0.220	0.184	0.737
Compound	Concentration, ppbv				
Acetylene					
1,3-Butadiene					0.460 (H)
Vinyl chloride					
Chloromethane					
Chloroethane					
Bromomethane					
Methylene chloride					
trans-1,2-Dichloroethylene					
1,1-Dichloroethane					
Chloroprene			0.460 (L)		
Bromochloromethane					
Chloroform					
1,1,1-Trichloroethane	1.145 (L)	1.275 (H)	1.590 (H)	0.937 (L)	1.622 (H)
Carbon tetrachloride	0.126 (L)	0.144 (L)	0.138 (L)	0.126 (L)	0.148 (L)
1,2-Dichloroethane					
Benzene	0.500 (H)	0.560 (H)	0.730 (H)	0.590 (H)	2.240 (H)
Trichloroethylene	0.337 (L)	0.310 (L)	0.391 (L)		0.768 (H)
1,2-Dichloropropane	1.510 (H)			0.100 (H)	0.500 (H)
Bromodichloromethane			0.120 (M)		
Toluene	2.010 (H)	2.140 (L)	2.690 (M)	2.270 (H)	11.490 (H)
n-Octane					0.340 (H)
cis-1,3-Dichloropropylene					
1,1,2-Trichloroethane					
Tetrachloroethylene	0.295 (L)	0.862 (L)	1.438 (L)	0.355 (M)	0.523 (M)
Dibromochloromethane					
Chlorobenzene					
Ethylbenzene	0.270 (M)	0.220 (M)	0.330 (L)	0.280 (H)	1.070 (H)
m/p-Xylene	0.980 (L)	1.040 (M)	1.330 (L)	1.260 (H)	6.240 (H)
Styrene/o-Xylene	0.650 (M)	0.590 (M)	0.730 (L)	0.750 (M)	2.720 (H)
Bromoform					
1,1,2,2-Tetrachloroethane					
m-Dichlorobenzene					
p-Dichlorobenzene					
o-Dichlorobenzene					
Propylene	1.260 (L)	1.170 (L)	0.920 (L)	1.770 (L)	8.100 (L)
trans-1,3-Dichloropropylene					
H High confidence level	M Medium confidence level	L Low confidence level	(Continued)		
D Duplicate sample	R Replicate sample				

TABLE H-2. NWNJ (Continued)

Sample ID	1323	1338	1357	1371	1380
Sample Date	8-1-90	8-2-90	8-6-90	8-8-90	8-30-90
Total NMOC, ppmC	0.608	0.330	0.066	0.432	0.585
Compound	Concentration, ppbv				
Acetylene					
1,3-Butadiene	0.140 (H)	0.110 (H)	0.210 (H)	0.170 (H)	0.180 (H)
Vinyl chloride					
Chloromethane					
Chloroethane	0.310 (L)			0.080	
Bromomethane					
Methylene chloride					
trans-1,2-Dichloroethylene					
1,1-Dichloroethane					
Chloroprene	0.450 (H)		0.640 (L)	0.200 (M)	0.030 (H)
Bromochloromethane					0.310 (M)
Chloroform					2.162 (H)
1,1,1-Trichloroethane	0.702 (L)	1.021 (H)	0.959 (L)	1.408 (H)	0.147 (L)
Carbon tetrachloride	0.149 (L)	0.144 (L)	0.136 (L)	0.177 (L)	
1,2-Dichloroethane					
Benzene	0.550 (H)	0.690 (H)	0.910 (H)	0.960 (H)	1.080 (H)
Trichloroethylene				0.104 (L)	0.974 (H)
1,2-Dichloropropane				0.230 (L)	0.320 (L)
Bromodichloromethane					
Toluene	2.440 (M)	5.010 (H)	3.470 (H)	4.520 (H)	7.240 (M)
n-Octane				0.330 (H)	
cis-1,3-Dichloropropylene					
1,1,2-Trichloroethane					
Tetrachloroethylene	0.381 (L)	0.397 (M)	0.135 (H)	0.337 (L)	3.728 (L)
Dibromochloromethane					
Chlorobenzene			0.070 (H)		
Ethylbenzene	0.190 (M)	0.310 (M)	0.410 (H)	0.490 (M)	0.540 (M)
m/p-Xylene	0.810 (M)	1.680 (M)	1.820 (H)	0.286 (H)	2.990 (M)
Styrene/o-Xylene	0.520 (M)	0.960 (M)	0.880 (M)	1.330 (M)	1.440 (M)
Bromoform					
1,1,2,2-Tetrachloroethane					
m-Dichlorobenzene					
p-Dichlorobenzene			0.500	1.680	
o-Dichlorobenzene					9.270 (L)
Propylene	1.640 (L)	2.350 (L)	2.320 (L)	7.090 (M)	4.170 (L)
trans-1,3-Dichloropropylene					
H High confidence level	M Medium confidence level		L Low confidence level		

TABLE H-3. MULTIPLE DETECTOR SPECIATED THREE-HOUR DATA SUMMARY FOR PLNJ

Sample ID	1279	1292D	1293D	1293R	1304
Sample Date	7-25-90	7-27-90	7-27-90	7-27-90	7-30-90
Total NMOC, ppmC	0.162	0.289	0.286	0.286	0.339
Compound					
Acetylene					
1,3-Butadiene		0.180 (H)			0.180 (H)
Vinyl chloride					
Chloromethane					
Chloroethane					
Bromomethane					
Methylene chloride					
trans-1,2-Dichloroethylene					
1,1-Dichloroethane					
Chloroprene	0.320 (L)	0.230 (M)	0.300 (L)	0.350 (L)	0.120 (H)
Bromochloromethane					
Chloroform					
1,1,1-Trichloroethane	0.484 (L)	0.957 (H)	0.938 (H)	1.000 (H)	0.695 (H)
Carbon tetrachloride	0.122 (L)	0.142 (L)	0.138 (L)	0.148 (L)	0.143 (L)
1,2-Dichloroethane					
Benzene	0.530 (H)	1.290 (H)	1.260 (H)	1.140 (M)	1.360 (H)
Trichloroethylene		0.088 (L)		0.222 (L)	
1,2-Dichloropropane		0.180 (H)	0.160 (M)		
Bromodichloromethane					
Toluene	1.090 (L)	3.840 (M)	3.520 (M)	3.190 (M)	3.130 (M)
n-Octane		0.070 (M)			
cis-1,3-Dichloropropylene					
1,1,2-Trichloroethane					
Tetrachloroethylene	0.387 (H)	0.691 (M)	3.001 (L)	3.130 (L)	0.186 (H)
Dibromochloromethane					
Chlorobenzene					
Ethylbenzene	0.150 (H)	0.320 (M)	0.350 (M)	0.340 (M)	0.320 (H)
m/p-Xylene	0.320 (L)	1.640 (H)	1.720 (M)	1.760 (H)	1.630 (H)
Styrene/o-Xylene	0.240 (H)	0.800 (H)	0.880 (M)	0.880 (M)	0.830 (H)
Bromoform					
1,1,2,2-Tetrachloroethane					
m-Dichlorobenzene	0.020 (L)				
p-Dichlorobenzene					
o-Dichlorobenzene					0.220 (L)
Propylene	0.650 (L)	1.970 (L)	1.690 (L)	1.660 (L)	4.050 (L)
trans-1,3-Dichloropropylene					
H High confidence level	M Medium confidence level	L Low confidence level	(Continued)		
D Duplicate sample	R Replicate sample				

TABLE H-3. PLNJ (Continued)

Sample ID	1308	1349	1350	1359	1380
Sample Date	7-31-90	8-3-90	8-6-90	8-8-90	8-7-90
Total NMOC, ppmC	1.165	0.899	0.066	0.319	1.079
Compound					
Acetylene				0.280 (H)	
1,3-Butadiene	0.470 (H)				
Vinyl chloride			0.060 (L)		
Chloromethane					
Chloroethane					
Bromomethane					
Methylene chloride		2.690 (H)	0.920 (H)		
trans-1,2-Dichloroethylene					
1,1-Dichloroethane					
Chloroprene	0.080 (L)	0.060 (M)		0.110 (H)	0.180 (M)
Bromochloromethane					
Chloroform		0.163 (M)			
1,1,1-Trichloroethane	12.323 (L)	0.322 (H)	0.190 (M)	0.961 (L)	0.369 (H)
Carbon tetrachloride	0.107 (L)	0.136 (L)	0.051 (L)	0.143 (L)	0.134 (L)
1,2-Dichloroethane					
Benzene	3.000 (H)	0.310 (H)	0.270 (H)	1.350 (H)	0.420 (H)
Trichloroethylene	0.344 (L)				
1,2-Dichloropropane	0.620 (H)	0.070 (H)			
Bromodichloromethane					
Toluene	13.340 (H)	1.280 (H)	0.900 (H)	3.850 (M)	0.780 (H)
n-Octane			0.004 (H)		
cis-1,3-Dichloropropylene					
1,1,2-Trichloroethane		0.140 (H)	2.910 (H)		
Tetrachloroethylene	0.543 (L)			0.186 (M)	0.162 (H)
Dibromochloromethane					
Chlorobenzene	0.080 (H)				0.010 (H)
Ethylbenzene	1.010 (H)	0.170 (L)	0.060 (H)	0.330 (H)	0.090 (H)
m/p-Xylene	4.840 (H)	0.520 (L)	0.320 (H)	1.710 (H)	0.380 (M)
Styrene/o-Xylene	2.400 (L)	0.300 (L)	0.160 (H)	0.950 (H)	0.210 (H)
Bromoform					
1,1,2,2-Tetrachloroethane					0.030 (M)
m-Dichlorobenzene					
p-Dichlorobenzene					
o-Dichlorobenzene					
Propylene	8.960 (L)	1.410 (M)	0.600 (L)	2.450 (L)	0.580 (L)
trans-1,3-Dichloropropylene					
H High confidence level	M Medium confidence level		L Low confidence level		

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/4- 91-008		2.		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE 1990 Nonmethane Organic Compound And Three-hour Air Toxics Monitoring Program				5. REPORT DATE January 1991	
7. AUTHOR(S) Radian Corporation Research Triangle Park, NC 27709				6. PERFORMING ORGANIZATION CODE	
				8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS				10. PROGRAM ELEMENT NO.	
				11. CONTRACT/GRANT NO. 68D80014	
12. SPONSORING AGENCY NAME AND ADDRESS Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, N.C. 27711				13. TYPE OF REPORT AND PERIOD COVERED	
				14. SPONSORING AGENCY CODE	
15. SUPPLEMENTARY NOTES					
16. ABSTRACT In certain areas of the country where the National Ambient Air Quality Standard (NAAQS) for ozone is being exceeded, additional measurements of ambient nonmethane organic compounds (NMOC) are needed to assist the affected States in developing revised ozone control strategies. Because of previous difficulty in obtaining accurate NMOC measurements, the U.S. Environmental Protection Agency (EPA) has provided monitoring and analytical assistance to these States, beginning in 1984 and continuing through the 1990 NMOC Monitoring Program.					
17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
Ozone Control Strategies National Ambient Air Quality Standards Nonmethane Organic Compound Monitoring Analysis 1990 NMOC Monitoring Program					
18. DISTRIBUTION STATEMENT Unlimited		19. SECURITY CLASS (This Report)		21. NO. OF PAGES 279	
		20. SECURITY CLASS (This page)		22. PRICE	
